

**2015-1983, -2001**

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**IN THE  
UNITED STATES COURT OF APPEALS  
FOR THE FEDERAL CIRCUIT**

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ORGANIK KIMYA AS,

*Appellant,*

v.

ROHM AND HAAS COMPANY,

*Appellee.*

**Appeal from the United States Patent and Trademark Office,  
Patent Trial and Appeal Board in Case Nos. IPR2014-00185  
and IPR2014-00350**

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**CORRECTED BRIEF FOR APPELLANT ORGANIK KIMYA AS**

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November 3, 2015

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## **CERTIFICATE OF INTEREST**

Counsel for Appellant Organik Kimya AS certify the following:

1. The full name of every party represented by us is:

Organik Kimya San. ve Tic. A.S.

2. The name of the real party in interest represented by us is:

Organik Kimya San. ve Tic. A.S.

3. All parent corporations and any publicly held companies that own 10 percent or more of the stock of the party represented by us are:

Organik Holding A.S.  
Chemorg Netherlands BV

4. The names of all law firms and the partners or associates that appeared for the party now represented by us in the trial court or agency or are expected to appear in this Court are:

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## STATEMENT OF RELATED CASES

No other appeal in or from the same proceeding in the U.S. Patent and Trademark Office (“PTO”) was previously before this or any other appellate court.

Rohm and Haas Company, Rohm and Haas Chemicals LLC, and The Dow Chemical Company (collectively, “Rohm and Haas”) have brought an action against Organik Kimya San. ve Tic. A.S., Organik Kimya Netherlands B.V., Organik Kimya U.S., Inc., Turk International LLC, and Aalborz Chemical LLC (collectively, “Organik”) for allegedly infringing U.S. Patent No. 6,020,435, U.S. Patent No. 6,252,004, and two related patents<sup>1</sup> before the United States International Trade Commission, Investigation No. 337-TA-883, captioned “In the Matter of Certain Opaque Polymers.” Separately, Rohm and Haas Company and Rohm and Haas Chemicals LLC have sued Organik Kimya San. ve Tic. A.S., Organik Kimya Netherlands B.V., and Organik Kimya U.S., Inc., alleging infringement of the same patents in the United States District Court for the District of Delaware, Case No. 13-cv-898.

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<sup>1</sup> U.S. Patent Nos. 7,435,783 and 7,803,878.



## **STATEMENT OF JURISDICTION**

This appeal is from the Final Written Decisions of the U.S. Patent and Trademark Office, Patent Trial and Appeal Board (“Board”), issued May 27, 2015, in Case No. IPR2014-00185, and June 26, 2015, in Case No. IPR2014-00350. In both decisions, the Board found that Appellant failed to establish that the challenged claims were unpatentable. The Board had jurisdiction to make these rulings under 35 U.S.C. §§ 6(c) and 318(a).

Appellant filed timely notices of appeal under 35 U.S.C. § 141 and 37 C.F.R. § 90.2 on July 27, 2015. This Court has jurisdiction under 28 U.S.C. § 1295(a)(4)(A) and 35 U.S.C. § 141(c).

## **I. STATEMENT OF THE ISSUES**

1. Did the Board err in construing “swelling agent” to mean “an aqueous or gaseous, volatile or fixed base, or combinations thereof, capable of permeating the shell and swelling the core, in the presence of the multistage polymer and monomer, under the conditions of the specific process for which the agent is to be used,” where the claims-at-issue merely recite providing or adding a “swelling agent” and do not recite a swelling *step*—let alone one that includes the additional limitations imported into the claim by the Board’s construction?

2. In addressing whether claims 1-5 of the ’435 patent are anticipated by Toda or rendered obvious by Touda, and whether claims 1-7 of the ’004 patent are rendered obvious by Toda in view of Crouch, did the Board err by applying an overly narrow construction of “swelling agent” and requiring that this limitation be proven by inherency?

## **II. STATEMENT OF THE CASE**

This appeal turns on the proper construction and application of “swelling agent” in claims 1-5 of the ’435 patent and claims 1-7 of the ’004 patent. Each of these claims recites a process for preparing emulsion polymer particles comprising the steps of (1) providing or adding an aqueous emulsion containing a multi-stage polymer, a monomer, and a “swelling agent”; and (2) reducing the monomer content to a certain level. The claims do *not* include a “swelling” step. Instead,

they require the addition of a “swelling agent” to the aqueous emulsion under conditions wherein there is no substantial polymerization of the monomer. Swelling can take place during a different (i.e., unclaimed) step and under conditions different from those recited in the claims. Indeed, swelling need not take place *at all* to satisfy these claims. All that is required is the addition of a “swelling agent,” i.e., an agent capable of swelling the multi-stage polymer particle under appropriate conditions.

The patentee purposely drafted these claims to cover certain intermediate steps of a larger process, such that infringement (and therefore validity) is judged by whether these specific steps are performed, *none* of which is a “swelling” step. Accordingly, for purposes of determining infringement and validity, it does not matter when or how—or even if—swelling occurs. If a known “swelling agent” is added to the claimed emulsion under the claimed conditions, then this limitation is satisfied regardless of what happens in other unclaimed steps. That is how the patentee chose to draft these claims (presumably to simplify proving infringement), and that is how they should be construed under the broadest-reasonable-interpretation standard.

Here, the asserted prior-art methods in U.S. Patent Nos. 5,360,827 (“Toda”) and 5,077,320 (“Touda”) disclose adding potassium hydroxide (KOH) or sodium hydroxide (NaOH) to a multi-stage polymer/monomer emulsion under conditions

where there is no substantial polymerization of the monomer. The common specification of the patents-in-suit acknowledges that “[s]uitable swelling agents include . . . fixed or permanent bases *such as potassium hydroxide . . . and the like.*” A35[8:45-52] (emphasis added). Thus, potassium hydroxide is expressly identified as a “swelling agent” in the claimed invention, and there is no dispute that sodium hydroxide is a fixed base with similar properties. Indeed, the specification admits that Toda discloses processes that “facilitate diffusion of base [e.g., potassium hydroxide] into the core of the polymer *in order to achieve swelling.*” A32[1:45-49] (emphasis added). Thus, Toda admittedly discloses a swelling agent.

The Board, however, erroneously adopted Rohm and Haas’s narrow construction of “swelling agent,” which essentially reads a swelling *step* into the claims by requiring that the claimed swelling agent be “capable of permeating the shell and swelling the core . . . under the conditions of the specific process for which the agent is to be used.” A9. This gave Rohm and Haas an opening to argue that potassium hydroxide and other fixed bases, such as sodium hydroxide—despite being described as “[s]uitable swelling agents” in the patents-in-suit—are not swelling agents in the Toda and Touda processes because they allegedly do not inherently (i.e., “*each and every time*”) permeate the shell and swell the core when the other (unclaimed) steps of those processes are carried out. A14. Rohm and

Haas sought to establish this alleged lack of inherency by having its paid expert perform variations of the Toda and Touda methods under modified conditions (e.g., a thousand-fold increase in particle quantity, reduced particle size, increased volume of emulsifier, deoxygenated conditions, a different addition technique, different drying conditions, etc.) that allegedly resulted in no swelling of the polymer core.

Having construed “swelling agent” improperly, the Board accepted Rohm and Haas’s irrelevant testing and concluded that potassium hydroxide and sodium hydroxide are not *inherently* “swelling agents” in the Toda and Touda processes, A16-18, 23-24, even though potassium hydroxide and other fixed or permanent bases are expressly described in the patents-in-suit as “[s]uitable swelling agents,” A34[8:45-52]. This was reversible error. The claims-at-issue do not recite a swelling step; therefore, Organik did not need to show that swelling *inherently* occurs in these prior-art processes “*each and every time*.” It was sufficient to show that a known swelling agent, suitable for use in the claimed invention, was added to an emulsion meeting all the other limitations of the claims.

For the reasons explained below, this Court should reject the Board’s narrow construction of “swelling agent” and reverse its ruling that claims 1-5 of the ’435 patent and claims 1-7 of the ’004 patent are not unpatentable.

### III. STATEMENT OF FACTS

#### A. The Common Specification of the '435 and '004 Patents

The '435 and '004 patents share a common specification directed to “aqueous emulsion polymerization processes for preparing polymer emulsions and emulsion polymers formed therefrom.” A32[1:8-11]. An “[e]mulsion polymer” is a “water-insoluble polymer which is prepared by emulsion polymerization techniques.” A32[1:12-14]. Emulsion polymers can include, but are not limited to, “hollow or voided emulsion polymers,” which have various applications in paints, paper coatings, inks, and the like.<sup>2</sup> A32[1:21-25, 10:10-18].

The specification acknowledges that “[v]oided latex particles can be prepared by any of several known process[es], including those described [in] U.S. Pat. No[.] . . . 5,360,827 [Toda].” A32[1:39-42]. Regarding Toda, the specification states:

Some of the [prior-art] processes, such as that described by U.S. Pat. No. 5,360,827 [Toda] describe the processes whereby, in the latter stages of polymerizing the shell, monomer is added to facilitate diffusion of base into the core of the polymer **in order to achieve swelling**. Then the pH of the emulsion is adjusted with a carboxyl-group containing monomer which is subsequently polymerized.

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<sup>2</sup> The claims-at-issue are not limited to voided/hollow particles but instead claim methods of preparing “emulsion polymer particles,” which include any water-insoluble polymer particle created via emulsion polymerization.

A32[1:45-51] (emphasis added). Thus, the specification admits that Toda discloses swelling of a polymer core via diffusion of a base, such as potassium hydroxide, into the core. The specification criticizes the Toda technique, however, as “time consuming” and not resulting in “suitable lightweight emulsion polymers.” A32[1:51-53].

The inventors of the patents-in-suit purportedly discovered an improvement over prior-art techniques for preparing emulsion polymer particles. As they explained: “Under the conditions of an emulsion polymerization, there is also an appreciable free-radical content, or radical flux, which keeps the polymerization process going. . . . When there is no appreciable free-radical content [in the system], . . . then no substantial amount of polymerization will occur.” A35[7:34-42]. Their purported invention was to add monomer and the swelling agent under conditions of “no substantial polymerization” of the monomer:

We have discovered that this free-radical content interferes with the extent of swelling which can be achieved. Previously known processes typically achieve swelling by adding a suitable swelling agent in the latter stages of charging the monomers which form the shell or at the completion of charging the monomers which form the shell. It is believed that the presence of unreacted monomer facilitates the transport of the swelling agent to the core. However, in previously known processes, the swelling agent was added to the system while there was still an appreciable free-radical content in the system. . . .

We have discovered that by providing an aqueous emulsion of the multi-stage emulsion polymer, monomer and swelling agent under conditions wherein there is no

substantial polymerization of the monomer, we can enhance the extent of swelling of the multistage emulsion polymer.

A35[7:43-60].

According to the specification, “[t]here are many means for providing that no substantial polymerization of monomer is occurring, including the addition of one or more polymerization inhibitors, the addition of one or more reducing agents, waiting for a sufficient period of time until there are no longer an appreciable number of free-radicals by virtue of them terminating, cooling the contents of the reactor to limit the reactivity of the free-radicals, and combinations thereof.” A35[7:61-8:1]. Thus, there are at least four different ways of achieving “no substantial polymerization of monomer,” including cooling the reaction mixture or waiting a sufficient period of time to diminish free radical activity.

The specification states that “[s]uitable swelling agents *include, are those which*, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core.” A35[8:40-42] (emphasis added). This passage is ambiguous because “include” is an open-ended term, whereas “are those which” is definitional. Thus, depending on which word is ignored, this sentence can have different meanings:



- Suitable swelling agents **include, are those which**, in the presence of the multi-stage emulsion polymer, are capable of permeating the shell and swelling the core.
- Suitable swelling agents **include, are those which**, in the presence of the multi-stage emulsion polymer, are capable of permeating the shell and swelling the core.

The specification further explains that “[s]welling agents may be aqueous or gaseous, volatile or fixed bases or combinations thereof.” A35[8:43-44]. More specifically, “[s]uitable swelling agents include . . . fixed or permanent bases such as *potassium hydroxide . . . and the like*.” A35[8:45-52] (emphasis added). Thus, the specification makes clear that potassium hydroxide and other fixed bases, such as sodium hydroxide, are suitable swelling agents in the context of the claimed invention.

The specification further states that it is preferable to add a swelling agent to the multi-stage emulsion polymer “at an elevated temperature, preferably at a temperature within 10° C. of the shell polymerization temperature.” A35-36[8:66-9:3]. This is because “[s]welling is generally very efficient under conditions of elevated temperature, in the presence of monomer and no substantial polymerization occurring.” A36[9:3-6]. On the other hand, one of the disclosed techniques for ensuring conditions of no substantial polymerization is “cooling the

contents of the reactor to limit the reactivity of the free-radicals.” A35[7:61-8:1]. Thus, the specification also envisions adding the swelling agent at a temperature low enough to substantially stop polymerization in the reactor. Swelling can then take place in a subsequent step under different conditions (e.g., at an elevated temperature).

## **B. The Claims-at-Issue**

Representative claim 1 of the '435 patent recites:

1. A process for preparing emulsion polymer particles comprising:
  - (a) providing an aqueous emulsion of
    - (i) multi-stage emulsion polymer, comprising a core stage polymer and a shell stage polymer, wherein the core stage polymer comprises, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core stage polymer, of hydrophilic monoethylenically unsaturated monomer, and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer; and wherein the shell stage polymer comprises, as polymerized units, at least 50 percent by weight of nonionic monoethylenically unsaturated monomer;
    - (ii) monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer; and
    - (iii) **swelling agent** under conditions wherein there is no substantial polymerization of the monomer; and
  - (b) reducing the level of monomer by at least fifty percent.

A49-50[36:55-37:10] (emphasis added).

Claim 1 of the '004 patent recites:

1. A process for preparing emulsion polymer particles comprising:
  - (a) providing an aqueous emulsion of
    - (i) multi-stage emulsion polymer, comprising a core stage polymer and a shell stage polymer, wherein the core stage polymer comprises, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core stage polymer, of hydrophilic monoethylenically unsaturated monomer, and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer; and wherein the shell stage polymer comprises, as polymerized units, at least 50 percent by weight of nonionic monoethylenically unsaturated monomer;
  - (b) adding an effective amount of one or more polymerization inhibitors or reducing agents to substantially stop any polymerization;
  - (c) providing monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer;
  - (d) adding **swelling agent**; and
  - (e) reducing the level of monomer by at least fifty percent.

A99[37:14-38:5] (emphasis added).

As can be seen, none of these process claims recites a “swelling” step. Instead, they require only the addition of a “swelling agent” to the claimed multi-stage polymer and monomer under conditions of no substantial polymerization.

Likewise, no claim in either patent expressly recites that the swelling agent must permeate and swell the core (as opposed to swelling other portions of the multi-stage polymer, such as the shell).<sup>3</sup> Indeed, these claims are not even limited to preparing hollow/voided particles but, instead, recite methods for preparing *any* type of “emulsion polymer particles,” whether hollow or not. Finally, the claims nowhere require that swelling must take place under any particular conditions.

### **C. The Asserted Prior-Art References**

#### **1. Toda (U.S. Patent No. 5,360,827)**

Toda discloses processes for the production of hollow particles that include copolymer particles, a monomer, and a base:

A process for preparation of latex of a hollow polymer which comprises adding a base, in the presence of a monomer, to latex containing carboxy-modified copolymer particles to make the pH of the latex 8 or more; adding a carboxyl group-containing monomer to make the pH of the latex 7 or less; and then polymerizing these monomers.

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<sup>3</sup> During the IPR proceedings, Rohm and Haas petitioned to add substitute claims that would have expressly recited a swelling agent permeating the shell and swelling the core. *See, e.g.*, A259 (seeking to amend original claim 3 of the '435 patent to recite the additional limitation “wherein said swelling agent permeates the shell and swells the core of the multi-stage emulsion polymer under said conditions of no substantial polymerization to form a swollen multi-stage emulsion polymer”; *see also* A3962 (proposing similar amendment to original claim 5 of the '004 patent)).

A629 at Abstract. Toda expressly teaches maintaining the carboxyl-group-containing monomer level between 0.1 and 40 percent to facilitate swelling during base treatment:

[I]t is preferable that the quantity of the carboxyl of group-containing monomer is, usually, in the range of 0.1 to 40 wt. % of the mixture of the total monomers. In case this use rate is below 0.1 wt. %, it is hard to swell the polymer particles with base treatment, and on the other hand, in case it is above 40 wt. %, a coagulate is liable to occur at the time of polymerization.

A631[3:14-21]. Toda also teaches carrying out base treatment in the presence of unreacted monomer to soften the polymer particles and promote diffusion of the base. A632[6:21-24].

Example 9 of Toda discloses a method of obtaining hollow polymer particles by first forming multi-stage emulsion particles having “a center layer, an intermediate layer, and a surface layer,” and then lowering the emulsion temperature to 20°C, thus creating a condition of no substantial polymerization of the monomer. A12 (citing Toda, A635[11:59-68]). Example 9 then creates hollow voids in the particles by

(i) adding 3 parts of styrene to the obtained latex-containing polymer particles to soften the particles, and then adding 30 parts of aqueous 10% potassium hydroxide solution and heating to 80° C for 3 hours (base treatment); (ii) adding 80 parts of aqueous 5% [methacrylic acid] and 50 parts of styrene and stirring the mixture at 80° C for 3 hours (acid treatment); and (iii) adding 10 parts of aqueous 3% [potassium sulfate]

solution, stirring the mixture of unreacted monomers at 80°C for 2 hours to carry out copolymerization, resulting in a polymerization conversion at this final stage of 99%.

A12-13 (citing Toda, A635[12:38-59]). Toda reports that this process results in hollow polymer particles with 390 nm voids and 30 nm shells. A635[12:56-59] (“The particle size and inner hole diameter of the obtained hollow polymer particles were observed and measured (photographic measurement). The results were shown in Table 2.”); *see also* A636, Table 2.

Example 11 of Toda discloses the same method as in Example 9, “except that the compositions of [the] monomer mixtures used for layers forming polymer particles and the rate of the seed particles were changed as shown in Table 2.” A635[12:62-66]. Toda reports that this process results in hollow polymer particles with 350 nm voids and 45 nm shells. A635[12:56-59]; A636, Table 2.

## **2. Touda (U.S. Patent No. 5,077,320)**

Touda discloses a process for “producing polymer particles containing one microvoid or two or more discrete microvoids.” A638 at Abstract. Like Toda, Touda expressly teaches that the amount of carboxyl-containing monomer is preferably from 0.1 to 40 percent of total monomer to facilitate “swelling of the copolymer particles.” A642[3:15-21]. Moreover, Touda teaches that an organic solvent should be chosen to facilitate swelling. A642[3:67-4:1] (“[A]ny organic

solvent may be used which can *fully swell the copolymer particles.*” (emphasis added)).

Touda discloses in Examples 1A and 1B the “[p]roduction of a microvoid-containing latex” by first forming multi-stage emulsion particles in an eight-hour process that allows polymerization to run to completion, such that there is no further substantial polymerization of the monomer. A20-21 (citing Touda, A643[6:51-67]). Then microvoids are formed by

charging the same reactor used in the production of the seed latex with 870 parts of deionized water, 100 parts of the filled polymer latex, 1 part of sodium dodecylbenzenesulfate, 30 parts of toluene, and 33 parts of a 10% aqueous solution of sodium hydroxide (‘NaOH’); stirring the mixture at 80° C for three hours; adding 300 parts of a 1% aqueous solution of hydrochloric acid; stirring the mixture at 80° C for 3 hours; cooling the reaction mixture to room temperature; and removing the organic solvent under reduced pressure.

A21 (citing Touda, A644[7:4-24]). Touda reported that this process results in polymer particles containing “1 to 2 small voids.” A644[7:19-21].

#### **D. Organik’s Petitions and the Board’s Institution Decisions**

Organik filed separate petitions to institute *inter partes* review (“IPR”) of the ’435 and ’004 patents. A100-65; A3808-67. In the ’435 Petition, Organik asserted that claims 1-5 of the ’435 patent are (1) anticipated by Toda, (2) rendered obvious by Touda, and (3) rendered obvious by U.S. Patent No. 4,910,229 (“Okubo”) in

view of Touda. A109-10. The Board instituted an IPR on the first two grounds. A181.

In its Institution Decision, the Board construed several limitations but did not construe “swelling agent,” finding that “no express claim construction is necessary” for that term. A173. The Board found there was reasonable likelihood that Organik would prevail on its assertion that claims 1-5 of the ’435 patent are anticipated by Toda and rendered obvious by Touda. A173-80. As for the “swelling agent” limitation, the Board found that Organik had “demonstrated sufficiently that Toda’s disclosure meets the claim limitation requiring ‘swelling agent under conditions wherein there is no substantial polymerization of the monomer.’” A176. The Board likewise found that Organik had “demonstrated adequately that Touda’s swelling step in Example 1 meets this limitation.” A180. At no point did the Board require a showing of inherency, i.e., that swelling occurs “*each and every time*” in these prior-art processes under varying conditions.

In the ’004 Petition, Organik asserted that (1) claims 1-6 are rendered obvious by Touda, (2) claim 7 is rendered obvious by Touda in view of U.S. Patent No. 5,292,660 (“Overbeek”), and (3) claims 1-7 are rendered obvious by Toda in view of U.S. Patent No. 2,574,020 (“Crouch”). A3817-18. The Board instituted



an IPR on each of these grounds.<sup>4</sup> A3876-86. The Board found no construction was necessary for “swelling agent,” A3876, and further found that Organik had adequately demonstrated that Toda satisfies this limitation, A3884-86.

## **E. The Board’s Final Decisions**

### **1. IPR2014-00185 (’435 Patent)**

After originally deciding in its Institution Decision that “swelling agent” requires “no express claim construction,” A173, the Board reversed course in its Final Written Decision and gave this two-word limitation a *44-word* construction, A9. The Board accepted Rohm and Haas’s argument that the claimed “swelling agent” must be capable of “permeating the shell and swelling the core,” even though that requirement is nowhere recited in the claims-at-issue, and even though other types of swelling are known, e.g., swelling of the shell. *See, e.g.*, A23 (citing Schork Decl., A2409-10, ¶ 128 (“[T]o the extent that any swelling occurred, it would take place in the shell.”)).

The Board rejected Organik’s argument that the specification indicates that suitable swelling agents *include* (but are not limited to) those capable of permeating the shell and swelling the core. *See* A8 (addressing the ambiguous “*include, are those which*” phrase in the specification (emphasis added) (citing

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<sup>4</sup> In this appeal, only the third ground (Toda in view of Crouch) is at issue. Organik does not appeal the Toda-based grounds for the ’004 patent.

A35[8:40-44])). According to the Board, “the Specification’s use of the word ‘include’ . . . is modified by the phrase immediately following it, i.e., ‘are those which,’ suggesting that suitable swelling agents include only those which exhibit the functional characteristic thereafter described.” A8-9. The Board cited no authority for this linguistic interpretation of the self-contradictory phrase “include, are those which.”<sup>5</sup> Nor did it cite any authority for the proposition that, when faced with an ambiguity about the meaning of a claim term, the “broadest reasonable interpretation” allows the Board to choose the *narrower* option.

Regarding Organik’s assertion that claims 1-5 of the ’435 patent are anticipated by Toda, the only element the Board identified as missing from Example 9 of Toda was the “swelling agent” limitation. A13; A18. For that limitation, the Board applied its narrow construction requiring that the swelling agent be “capable of permeating the shell and swelling the core, in the presence of the multistage polymer and monomer, under the conditions of the specific process for which the agent is to be used.” A14. The Board then reasoned that “Petitioner has neither asserted nor shown that Toda *expressly* teaches that potassium hydroxide permeates the shell and swells the core of the multi-stage polymer in Toda’s Example 9.” *Id.* As the Board acknowledged, however, Organik’s main

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<sup>5</sup> Indeed, Rohm and Haas’s expert, Dr. Schork, testified that this portion of the specification contains a typographical error. A981-83[21:16-23:3].

argument was that “Toda discloses a ‘swelling agent’ *expressly, not inherently*, by disclosing potassium hydroxide in Example 9.” *Id.* (emphasis added). Nevertheless, because the Board adopted a narrow construction importing several additional limitations from the specification (e.g., “permeating the shell,” “swelling the core,” “under the conditions of the specific process,” etc.), it converted Organik’s “express” argument into an “inherency” argument. A14-15 (“In other words, Petitioner’s argument is that Toda *inherently* discloses that potassium hydroxide is capable of permeating the shell and swelling the core of the polymer particles in Toda’s Example 9.”).

The Board then accepted the test results of Rohm and Haas’s paid expert, Dr. Schork, which purportedly show that Example 9 of Toda—*contrary to what is actually reported in Toda*—yields only an “unprocessible lump of coagulum” that is “incompatible with the final ‘hollow’ sphere morphology reported [by Toda]” and exhibits “no observable swelling.” A2400, ¶ 103. Dr. Schork opined that his test results “call into question the authenticity of the entire [Toda] patent.” A2402-03, ¶ 108. In other words, Dr. Schork essentially accused the Toda inventors of submitting fraudulent test results and photographs to the PTO showing the formation of hollow particles in Example 9. *Compare* A2400, ¶ 103 (asserting that Example 9 does not work), *with* Toda, A635[12:56-59] (reporting for Example

9 that “[t]he particle size and inner hole diameter of the obtained hollow polymer particles were observed and measured (photographic measurement)”).

The Board credited Dr. Schork’s testimony, which questioned “the authenticity of the entire [Toda] patent,” and dismissed the testimony of Organik’s expert, Dr. Prud’homme, who identified numerous deficiencies in Dr. Schork’s test methodology. Based on its narrow construction of “swelling agent” and its insistence on proof of inherency, the Board concluded that Organik failed to show that “Toda discloses potassium hydroxide as a ‘swelling agent’ in the process of Example 9.” A18.

Regarding Organik’s assertion that claims 1-5 of the ’435 patent would have been obvious in view of Touda, the Board again relied only on the “swelling agent” limitation to reject this argument. A21-22. The Board’s reasoning was identical to that described above for Toda. Again, the Board relied on testing performed by Rohm and Haas’s paid expert, which purported to show—*contrary to what Touda actually reported and corroborated with photographic evidence and data*—that “there were no microvoid-containing latexes formed by the procedure set forth in Example 1 of the Touda ‘320 patent,” A2417, ¶ 150, and therefore no swelling of the core, A2417, ¶ 151.

## **2. IPR2014-00350 ('004 Patent)**

The Board's analysis in the '004 patent IPR proceeded along largely the same lines as the '435 patent IPR and again hinged on the Board's narrow construction of "swelling agent." The Board initially decided in its Institution Decision that "no express claim construction is necessary" for "swelling agent," A3876, but reversed course in its Final Written Decision and gave the term the same lengthy construction as in the '435 patent IPR, A59. The Board applied the same reasoning, rejecting Organik's argument that the specification states that suitable swelling agents include, but are not limited to, those capable of permeating the shell and swelling the core. A58-59. And the Board again concluded that "swelling agent" is limited to compounds capable of permeating the shell and swelling the core "in the presence of the multistage polymer and monomer, under the conditions of the specific process for which the agent is to be used," even though the challenged claims of the '004 patent do not recite "permeating the shell" or "swelling the core," or even forming hollow particles. A59.

As to Organik's argument that the '004 patent claims would have been obvious over the combination of Toda and Crouch, the only element the Board identified as missing from the combination was the "swelling agent" limitation. A70; A74. The Board rejected Organik's argument that Toda expressly discloses a swelling agent because it teaches adding potassium hydroxide (KOH), which the

'004 patent states is a suitable swelling agent. A70-72. The Board, relying on its narrow construction of “swelling agent,” noted that although Toda discloses using potassium hydroxide, it does not specifically state that potassium hydroxide will cause swelling by permeating the polymer shell and swelling the core. A71.

The Board again converted Organik’s argument that Toda *expressly* teaches adding a swelling agent into an inherency argument, as it did in the ’435 patent IPR. A72. The Board thus required Organik to provide evidence that the potassium hydroxide used in Toda would inherently permeate the shell and swell the core under specific process conditions, and it discounted Toda’s express disclosure of adding potassium hydroxide in a process for producing hollow emulsion polymers. The Board relied on the testimony of Rohm and Haas’s expert, Dr. Schork, who performed an altered version of the Toda process. The Board accepted Dr. Schork’s results, which allegedly show that Toda’s process “did not result in voided or swollen emulsion particles,” or even produce “multi-stage emulsion particles with a separate core and shell,” A73 (quoting Schork Decl., A4750-51, ¶ 120), even though the ’004 patent *expressly admits* that Toda discloses swelling of the core to produce hollow particles, A81[1:47-51]. The Board thus accepted Dr. Schork’s testimony that Toda’s disclosure of producing swollen emulsion particles was fraudulent. Applying its narrow construction of “swelling agent” in the context of inherency, the Board concluded that Organik

failed to establish that the potassium hydroxide used in Toda's examples inherently permeated the shell and swelled the core.

#### **IV. SUMMARY OF THE ARGUMENT**

##### **1. The Board incorrectly construed "swelling agent"**

The Board's narrow construction of "swelling agent" improperly reads a swelling step into the claims even though no such step is required. The claimed processes require only adding or providing a "swelling agent"; they do not recite a swelling step or process conditions that would facilitate swelling. Thus, for purposes of determining validity or infringement, all that is required is the addition of a known swelling agent under the claimed conditions. Once that step occurs, the analysis for this limitation ends. Swelling, to the extent it occurs at all, can take place in a subsequent (unclaimed) step and under different conditions.

The Board's construction also improperly departs from the plain meaning of "swelling agent" by limiting it to compounds "capable of permeating the shell and swelling the core . . . under the conditions of the specific process for which the agent is to be used." The claims do not require that the claimed swelling agent be capable of permeating the shell and swelling the core under specific process conditions. The Board arrived at this construction by selecting the *narrower* of two possible interpretations of a grammatically ambiguous passage in the specification, contrary to the broadest-reasonable-interpretation rule. The Board's

construction improperly excludes other possible mechanisms of swelling, such as swelling of the shell.

2. The Board erred in requiring that “swelling agent” be proven by inherency

As a result of its erroneous claim construction, the Board ignored the express disclosure of “swelling agents” in the Toda and Touda references and concluded that neither reference teaches this limitation. Both Toda and Touda disclose processes for producing hollow or voided polymer particles, in which a base such as potassium hydroxide is used to permeate the polymer particles and cause swelling. *See, e.g.,* A631[3:56-61]; A632[6:7-11]; A632-33[6:68-7:4]; A642[4:36-53]; A644[7:4-24]. The patents-in-suit describe potassium hydroxide as a “[s]uitable swelling agent[.]” A35[8:45-52]. Both Toda and Touda report experimental data showing the diameter of the voids produced in the hollow polymer particles, and Touda even includes photos of the hollow particles produced. *See* A636, Table 2; A639, Fig. 1(a); A645, Table 1. Yet despite this express disclosure, the Board concluded that Toda and Touda do not disclose a swelling agent because they allegedly fail to expressly disclose that potassium hydroxide or sodium hydroxide cause swelling by permeating the shell of the polymer and swelling the core. A18; A21-22; A66-67.

Based on this erroneous finding and the erroneous construction of “swelling agent,” the Board required Organik to prove that Toda and Touda *inherently*



disclose that potassium hydroxide or sodium hydroxide permeates the polymer shell and swells the core, i.e., does so “*each and every time.*” A14-15. The Board then compounded its errors by relying on flawed testing by Rohm and Haas’s expert, Dr. Schork, and accepting his argument that Toda’s and Touda’s experimental results are fraudulent. By applying an overly narrow claim construction and requiring proof by inherency, the Board reached the erroneous conclusion that the claims-at-issue are not unpatentable over Toda and Touda.

## **V. LEGAL STANDARDS**

### **A. Standard of Review**

This Court reviews the Board’s claim construction de novo and any underlying factual determinations concerning extrinsic evidence for substantial evidence. *In re Cuozzo Speed Techs., LLC*, 793 F.3d 1268, 1279-80 (Fed. Cir. 2015); *see also Teva Pharm. USA, Inc. v. Sandoz, Inc.*, 135 S. Ct. 831 (2015). Where, as here, the Board’s claim construction is based solely on intrinsic evidence, review is de novo. *See, e.g., Microsoft Corp. v. Proxyconn, Inc.*, 789 F.3d 1292, 1297 (Fed. Cir. 2015) (“In this case, because the intrinsic record fully determines the proper construction, we review the Board’s claim constructions de novo.” (citing *Teva*, 135 S. Ct. at 840-42)).

Anticipation is a question of fact, while obviousness is question of law based on several underlying factual inquiries. *Kennametal, Inc. v. Ingersoll Cutting Tool*

*Co.*, 780 F.3d 1376, 1381 (Fed. Cir. 2015). This Court reviews the Board’s legal determinations without deference and its factual findings for substantial evidence.

*Id.*

## **B. Legal Standards Relating to Broadest Reasonable Construction**

In an IPR proceeding, a claim “shall be given its broadest reasonable construction in light of the specification of the patent in which it appears.” *In re Cuozzo*, 793 F.3d at 1275 (quoting 37 C.F.R. § 42.100(b)). Giving claims their broadest reasonable construction “serves the public interest by reducing the possibility that claims, finally allowed, will be given broader scope than is justified.” *In re Yamamoto*, 740 F.2d 1569, 1571 (Fed. Cir. 1984). The construction of a claim term under the broadest reasonable standard “may be the same as or broader than the construction of a term under the *Phillips* standard. But it cannot be narrower.” *Facebook, Inc. v. Pragmatus AV, LLC*, 582 F. App’x 864, 869 (Fed. Cir. 2014) (nonprecedential).

The words of a patent claim are generally given their ordinary and customary meaning, as understood by a person of ordinary skill in the art when read in the context of the specification and prosecution history. *Phillips v. AWH Corp.*, 415 F.3d 1303, 1312-13 (Fed. Cir. 2005) (en banc). There are two exceptions to this general rule: (1) when a patentee acts as his own lexicographer and sets out a definition or (2) when the patentee disavows the full scope of a claim

term, either in the specification or during prosecution. *Thorner v. Sony Comput. Entm't Am. LLC*, 669 F.3d 1362, 1365 (Fed. Cir. 2012).

Where there is no clear lexicography or disavowal, claim terms should be given their ordinary meaning. Indeed, “it is improper to read limitations from a preferred embodiment described in the specification—even if it is the only embodiment—into the claims absent a clear indication in the intrinsic record that the patentee intended the claims to be so limited.” *Liebel-Flarsheim Co. v. Medrad, Inc.*, 358 F.3d 898, 913 (Fed. Cir. 2004); *see also In re Bigio*, 381 F.3d 1320, 1325 (Fed. Cir. 2004) (“Absent claim language carrying a narrow meaning, the PTO should only limit the claim based on the specification or prosecution history when those sources expressly disclaim the broader definition.”).

Where a claim term is ambiguous, that ambiguity should be resolved against the drafter (i.e., the patentee). *See, e.g., Athletic Alternatives, Inc. v. Prince Mfg., Inc.*, 73 F.3d 1573, 1581 (Fed. Cir. 1996) (construing an ambiguous term against the patentee in the context of infringement). When interpreting claims involved in an IPR under the “broadest reasonable interpretation” standard, this means ambiguity should be resolved so as to give claim terms the broader meaning supported by the claim language and specification. In other words, when two reasonable constructions are possible, the broadest-reasonable-interpretation standard mandates that the Board choose the broader construction. *See, e.g., In re*

*Hyatt*, 211 F.3d 1367, 1372-73 (Fed. Cir. 2000) (affirming the Board’s adoption of the broader of two possible constructions under the “broadest reasonable” standard).

### **C. Legal Standards Relating to Inherency**

Anticipation may be proven by showing that all of the claim limitations are either expressly or inherently disclosed in a prior-art reference. *See, e.g., In re Cruciferous Sprout Litig.*, 301 F.3d 1343, 1349 (Fed. Cir. 2002). In order to establish inherency, a party must show that the alleged inherent characteristic results from a given set of circumstances each and every time. *See, e.g., Cont’l Can Co. USA v. Monsanto Co.*, 948 F.2d 1264, 1268-69 (Fed. Cir. 1991) (“Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing *may* result from a given set of circumstances is not sufficient.” (quoting *In re Oelrich*, 666 F.2d 578, 581 (CCPA 1981))).

Because an anticipatory reference can disclose a limitation either expressly or inherently, a reference that expressly discloses a limitation need not also disclose that limitation inherently. *Cf. In re Cruciferous Sprout Litig.*, 301 F.3d at 1349 (“It is well settled that a prior art reference may anticipate when the claim limitations *not expressly found* in that reference are nonetheless inherent in it.” (emphasis added)). Accordingly, inherency should only be applied when a reference is silent as to a particular limitation. *See, e.g., Cont’l Can*, 948 F.2d at

1268 (stating that inherency may be applied, and a reference may “serve as an anticipation *when the reference is silent* about the asserted inherent characteristic” (emphasis added)).

## **VI. ARGUMENT**

### **A. The Board Erred in Its Construction of “Swelling Agent”**

#### **1. The Board’s Construction Improperly Imports a Swelling Step into the Claims**

The Board’s construction of “swelling agent” improperly reads a swelling step into the claims despite the fact that no such step is recited or required. Every claim of the ’435 and ’004 patents recites a “process for preparing emulsion polymer particles comprising” certain method steps. None of these method claims, however, recites a swelling step or requires reaction conditions in which swelling would occur. Instead, the claims merely require providing or adding a swelling *agent*. Once a known swelling agent has been provided or added under the claimed conditions, the analysis as to that limitation is completed. Although a “swelling agent” must, of course, be capable of swelling the polymer particles under appropriate conditions, the claims do not *require* swelling to occur. Because the claims recite processes “comprising” certain steps, swelling may be an additional, unclaimed step within the scope of the claims but is not required.

Nor do the claims require that the emulsion polymer particles prepared through the claimed processes be “hollow or voided emulsion polymers,” i.e.,

swollen-core emulsion polymers. Indeed, the specification teaches that hollow or voided polymers are just one type of emulsion polymer. *See, e.g.*, A32[1:21-23]. Instead, the claims broadly recite a “process for preparing emulsion polymer particles” with no requirement that they be *swollen* emulsion particles, let alone hollow or voided particles produced by swelling the core. By contrast, other patents in the same family as the ’435 and ’004 patents specifically claim processes for producing a “*swollen* multi-stage emulsion polymer.” *See, e.g.*, A666 (quoting U.S. Patent No. 7,803,878, claim 1). So Rohm and Haas certainly knows how to claim a swelling step when it wants to.

Rohm and Haas is a sophisticated chemical company that knows how to draft process claims to cover *precisely* the steps it wants, and nothing more. Here, the claims-at-issue were specifically drafted to cover only certain intermediate, *pre-swelling* steps of a larger process for producing emulsion polymer particles. An intermediate process that produces *un-swollen* emulsion polymer particles, for example, would still fall within the scope of these claims, provided that the recited method steps have been performed. Those un-swollen particles could later be swollen in an unclaimed process step, but this is not required by the claims-at-issue. Rohm and Haas presumably drafted the claims in this manner for a reason, *e.g.*, to make it easier to prove infringement or to avoid concerns about subsequent processing steps occurring outside the United States. Whatever its reason, Rohm

and Haas expressly chose to draft claims on an intermediate process that *does not include a swelling step* and does not require the formation of swollen or hollow particles.

This Court considered a similar claim construction issue in *Cadence Pharmaceuticals Inc. v. Exela PharmSci Inc.*, 780 F.3d 1364 (Fed. Cir. 2015). The claims at issue in *Cadence* recited a “stable, liquid formulation” of acetaminophen “dispersed in an aqueous medium containing *a buffering agent*.” *Id.* at 1367. The Court rejected Exela’s argument that a “buffering agent” must be present “in an effective concentration to resist material changes in pH,” explaining that it saw “nothing in the intrinsic record to warrant adding requirements of effective concentration or resistance to material [pH] change.” *Id.* at 1369 (citation omitted). The Court held that a “buffering agent” is merely an “agent that helps the formulation resist change in pH,” and does not include any functional limitation regarding the extent to which the “buffering agent” actually buffers the formulation, i.e., that it resist *material* changes in pH. *Id.* In other words, although a “buffering agent” must be capable of buffering a formulation, it need not achieve any particular functional result unless the claim language or intrinsic record clearly supports limiting the claim in that fashion.

Even district courts, which do not apply the broadest-reasonable-interpretation standard, have construed similar terms and declined to read in

functional limitations from the specification. In *Procter & Gamble Co. v. McNeil-PPC, Inc.*, for example, the district court held that a “gelling agent” must have the ability to cause another substance to gel but does *not* require that a gel actually be formed in every instance. No. 08-CV-251-BBC, 2009 WL 196826, at \*8 (W.D. Wisc. Jan. 26, 2009). The court thus rejected the contention that “an agent is a gelling agent only when it forms a gel.” *Id.*

Here, the Board’s construction is wrong because it reads a swelling step into the claims even though no such step is recited.<sup>6</sup> The Board not only required that a “swelling agent” be capable of causing swelling in one specific fashion (i.e., “permeating the shell and swelling the core”), but also that a swelling agent must be capable of doing so “specifically under the conditions of the specific process for which the agent is to be used.” A9. The Board thus narrowed the claims to processes in which reaction conditions are suitable for swelling and, in turn, limited “swelling agents” solely to compounds that would actually cause swelling of the core under those conditions. The claims, however, do not require swelling of the core or conditions that would enable such swelling. As in *Cadence* and *Procter & Gamble*, it is improper to read this functional limitation into the claims,

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<sup>6</sup> Rohm and Haas’s expert, Dr. Schork, admitted that he was implicitly reading a swelling step into the claims. A980 (“Q: So you’re reading a swelling step into the claim? A: Yes.”).



and the Board thus erred by limiting the scope of “swelling agent” based on an unclaimed swelling step or unclaimed process conditions.

**2. In Construing “Swelling Agent,” the Board Erroneously Imported Limitations from the Specification into the Claims**

**a. The Claims Are Not Limited to Swelling Agents “Capable of Permeating the Shell and Swelling the Core”**

The ’435 and ’004 patent claims recite providing or adding a “swelling agent” and do not further limit or define the term. The shared specification explains that “[s]welling agents may be aqueous or gaseous, volatile or fixed bases or combinations thereof.” A35[8:43-44]. The specification outlines several volatile bases and fixed or permanent bases that are included within the universe of possible swelling agents:

*Suitable swelling agents include volatile bases* such as ammonia, ammonium hydroxide, and volatile lower aliphatic amines, such as morpholine, trimethylamine, and trimethylamine, and the like; *fixed or permanent bases such as potassium hydroxide*, lithium hydroxide, zinc ammonium complex, copper ammonium complex, silver ammonium complex, strontium hydroxide, barium hydroxide and the like.

A35[8:45-52] (emphases added). The specification thus expressly defines “[s]uitable swelling agents” to include fixed or permanent bases, such as potassium hydroxide or sodium hydroxide. *Id.*

Although the claims do not state that the swelling agent must be “capable of permeating the shell and swelling the core,” or even include a swelling step, the Board read this limitation into the claims based on a grammatically ambiguous passage from the specification, choosing the *narrower* of the two possible interpretations of the passage. The specification states that “[s]uitable swelling agents *include, are those which*, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core.” A35[8:40-42] (emphasis added). This passage is ambiguous because “include” is an open-ended term, whereas “are those which” is definitional and closed. As a result, this passage can have different meanings depending on whether the reader ignores the word “include” or the word “are.” If neither word is ignored, the passage is self-contradictory and nonsensical.

Although the Board purported to consider the word “include” in this passage, its construction of “swelling agent” reveals that it ignored the word “include” entirely. The Board stated, for example, that “the Specification’s use of the word ‘include,’ in this instance, is modified by the phrase immediately following it, i.e., ‘are those which,’ suggesting that suitable swelling agents *include only those which* exhibit the functional characteristic thereafter described.” A8-9 (emphasis added). But if suitable swelling agents include *only* those compounds

which exhibit the functional characteristic and no others, the word “include” is superfluous.

The Board erred by departing from the broad, plain meaning of “swelling agent” based on this ambiguous specification passage, which does not “clearly set forth a definition of the disputed claim term” and thus does not rise to the level of clear lexicography. *See, e.g., Thorner*, 669 F.3d at 1365 (quoting *CCS Fitness, Inc. v. Brunswick Corp.*, 288 F.3d 1359, 1366 (Fed. Cir. 2002)). By doing so, the Board improperly excluded embodiments that fall within the plain meaning of “swelling agent.” For example, the Board credited Dr. Schork’s testimony that a fixed base such as sodium hydroxide could cause swelling even if it fails to permeate the shell and swell the core, swelling the polymer shell rather than the core. A23 (citing Schork Decl., A2409-10, ¶ 128). Furthermore, the specification of the patents-in-suit states that solvents “may be added to aid in fixed or permanent base penetration” of the polymer particles, indicating that a swelling agent need not, on its own, be singularly capable of permeating the shell. A35[8:52-56].

The Board’s construction is erroneous because, by limiting the claim to the *narrower* of two possible interpretations of the specification, the Board failed to apply the broadest-reasonable-interpretation standard. *See In re Cuozzo*, 793 F.3d at 1275. Here, the broadest reasonable interpretation consistent with the

specification is that suitable swelling agents include, *but are not limited to*, compounds “capable of permeating the shell and swelling the core.” Such compounds include those that swell the emulsion polymers in some other fashion, such as by swelling the shell, or which are capable of permeating the shell and swelling the core only if aided by a solvent.

Holding that swelling agents include but are not limited to compounds “capable of permeating the shell and swelling the core” also comports with the canon of construction that ambiguous language should be resolved against the drafter. *See, e.g., Athletic Alternatives*, 73 F.3d at 1581 (resolving ambiguous claim language against patentee in the context of infringement); *see also 3M Innovative Props. Co. v. Tredegar Corp.*, 725 F.3d 1315, 1336 (Fed. Cir. 2013) (Plager, J., concurring) (“When a term is ambiguous, a crystal ball matter, the ambiguity should be construed against the draftsman. (Or better yet, the claim should simply be invalidated as indefinite, though our court has not seen fit to go there as yet.)”). Here, this principle dictates that the ambiguous specification passage should be read broadly such that it does not narrow the scope of the term “swelling agent.”

**b. The Claims Are Not Limited to Swelling Agents Capable of Permeating the Shell and Swelling the Core “Under the Conditions of the Specific Process for Which the Agent Is To Be Used”**

Because the claims do not recite a swelling step or require conditions that facilitate swelling, they also do not require that the swelling agent be capable of causing swelling under any particular conditions. Although the swelling agent is *added* “under conditions wherein there is no substantial polymerization of the monomer,” the claims do not require that the swelling agent be capable of *causing swelling* under those same conditions. Instead, the swelling agent could be added under conditions wherein there is no substantial polymerization of the monomer and the process conditions could then be altered in one or more unclaimed process steps, such as increasing the reaction temperature or adding a suitable solvent. Based on the broad method claims at issue here, all that is required is the addition of a known swelling agent that is capable of causing the polymers to swell under *appropriate* process conditions, not necessarily the same conditions that result in no substantial polymerization of the monomer.

The Board’s construction improperly excludes preferred embodiments disclosed in the specification by narrowing “swelling agents” to compounds capable of permeating the shell and swelling the core under specific, unclaimed reaction conditions. For example, the specification of the patents-in-suit teaches that there “are many means for providing that no substantial polymerization of

monomer is occurring, including . . . cooling the contents of the reactor to limit the reactivity of the free-radicals.”<sup>7</sup> A35[7:61-8:1]. The Board even construed the “conditions wherein there is no substantial polymerization of the monomer” to include those caused by “cooling the contents of the reactor to limit the reactivity of the free-radicals.” *See* A10-11 (citing A35[7:61-8:1]).

Despite this disclosure and claim construction, the Board accepted Rohm and Haas’s argument that a compound could not be a “swelling agent” under such conditions because decreasing the temperature would render the polymer shell too hard to be permeated. *See, e.g.*, A15. The Board’s construction thus excludes these embodiments because the lower temperatures used to ensure no substantial polymerization of the monomer can also impair swelling. The Board improperly departed from the claim’s plain meaning in the absence of any lexicography or disavowal to support narrowing “swelling agents” in this fashion. *Thorner*, 669 F.3d at 1365. A claim construction that excludes a preferred embodiment disclosed in the specification is “rarely, if ever, correct and would require highly

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<sup>7</sup> Rohm and Haas highlighted the importance of cooling during prosecution of the ’435 patent. Rohm and Haas argued in response to a validity rejection that “[s]pecific required process condition[s],” including “no substantial polymerization of the monomer,” was one of two “critical and claimed features” of the alleged invention. A758. Rohm and Haas specifically cited the specification passage describing cooling the reactor contents as a way of ensuring “no substantial polymerization of the monomer” and stated that this specification passage “explained the criticality” of the two “critical and claimed features.” *Id.*

persuasive evidentiary support.” *Vitronics Corp. v. Conceptronic, Inc.*, 90 F.3d 1576, 1583 (Fed. Cir. 1996). The Board thus erred by adopting a construction that implicitly narrows “swelling agent” to compounds that cause swelling under conditions wherein there is no substantial polymerization of the monomer and excludes preferred embodiments disclosed in the specification.

**B. The Board Erred in Applying Its Narrow Construction of “Swelling Agent” to the Validity Analysis and Requiring Proof by Inherency Even Though Toda and Touda *Expressly* Disclose the Addition of a Known Swelling Agent**

**1. The Board Erred by Requiring Proof That Toda and Touda *Inherently* Disclose a “Swelling Agent” Where the References *Expressly* Disclose That Limitation**

Based on its narrow construction of “swelling agent,” the Board ignored the express disclosure in Toda and Touda of using potassium hydroxide and sodium hydroxide as swelling agents to produce hollow emulsion polymers. The Board reasoned that Toda and Touda do not expressly disclose that potassium hydroxide and sodium hydroxide achieve swelling by permeating the shell and swelling the core under specific process conditions. *See, e.g.*, A18; A21-22; A66-67. The Board thus required Organik to show that potassium hydroxide and sodium hydroxide *inherently* permeate the shell and swell the core, i.e., that they do so “*each and every time*,” A14-15, under process conditions not required by the claims-at-issue.

Toda and Touda expressly disclose using potassium hydroxide or sodium hydroxide, which are described in the patents-in-suit as “[s]uitable swelling agents,” in processes for producing hollow or voided emulsion polymers. *See supra* Section III.C; *see also* A35[8:45-52]. Given this express disclosure of a “swelling agent” in Toda and Touda, the Board erred by converting Organik’s argument into one of inherency. Where, as here, a limitation is expressly disclosed in a prior-art reference, the Board should not require proof by inherency. *See, e.g., Cont’l Can*, 948 F.2d at 1268 (stating that inherency may be applied to fill a “gap in the reference,” i.e., “when the reference is silent about the asserted inherent characteristic”).

Because of this error, the Board improperly imposed a heightened burden of proof on Organik. Specifically, by requiring proof by inherency, the Board required Organik to show that the potassium hydroxide and sodium hydroxide in Toda and Touda permeate the shell and swell the core *each and every time*, rather than requiring that they merely meet the Board’s (albeit erroneous) construction of being “*capable of* permeating the shell and swelling the core.” A14-15 (emphasis added). The Board thus further restricted its already narrow claim construction, limiting “swelling agent” to a compound that not only is capable of swelling, but that inevitably causes swelling “*each and every time.*” A14.



As discussed above, the '435 and '004 patent claims do not recite a swelling step or require specific process conditions that are suitable for swelling. Instead, the claims require only adding or providing a “swelling agent” and thus do not require that the swelling agent actually cause swelling, much less that it cause swelling in a particular fashion or “*each and every time*.” If a compound is capable of causing swelling under *any* suitable conditions, it is a “swelling agent” as defined in the patents-in-suit. The Board thus erred by converting Organik’s express disclosure argument into an inherency argument and requiring Organik to show that the potassium hydroxide and sodium hydroxide taught in Toda and Touda inevitably cause swelling “*each and every time*” by permeating the shell and swelling the core under specific reaction conditions.

**2. The Board Ignored Toda’s and Touda’s Express Disclosure of Using “Swelling Agents” to Produce Hollow Polymer Particles**

**a. Toda Expressly Discloses Using Bases Such as Potassium Hydroxide or Sodium Hydroxide to Produce Hollow Polymer Particles**

Toda discloses a process for preparing hollow polymer particles, which includes adding a base in the presence of the monomer:

***[A] process for preparation of latex of a hollow polymer which comprises adding a base***, in the presence of a monomer, to latex containing carboxy-modified copolymer particles to make the pH of the latex 8 or more; adding a carboxyl group-containing monomer to

make the pH of the latex 7 or less; and then polymerizing these monomers.

A630[2:34-41] (emphasis added).

Toda explains that “hollow polymer particles are prepared by adding a base to the above latex containing the polymer particles to make the pH of the latex 8 or more (base treatment step)” and then adding an acid to lower the pH again. A632[6:7-11]. Toda teaches that “[u]sable bases are not particularly limited” and include “alkali metal hydroxides such as sodium hydroxide, potassium hydroxide and lithium hydroxide; ammonia; amine compounds such as dimethylamine and diethanolamine; etc.” A632-33[6:68-7:4].

Toda also expressly teaches that this base treatment step is used to swell the polymer particles. For example, Toda expressly discloses using a certain amount of the carboxyl group-containing monomer (0.1 to 40 wt. %) to make it easier for the base treatment step to swell the polymer particles. A631[3:12-17]. Toda uses this range because, with quantities “below 0.1 wt. %, it is hard to swell the polymer particles with base treatment.” A631[3:17-19].

As the Board itself found, Toda’s Example 9 discloses a method of forming “*hollow* polymer particles” with a center layer, an intermediate layer, and a surface (or shell) layer. A12 (emphasis added) (citing A635[11:59-68]). After these three layers are formed, the temperature is lowered to 20°C, which creates a condition of no substantial polymerization, as required by the claims-in-suit. A635[12:34-36].

At this low temperature, potassium hydroxide is added and the mixture is then heated to 80°C during the so-called base treatment, where swelling occurs to form the hollow particles. A635[12:40-44]. Thereafter, the polymerization process is completed. A635[12:47-56].

Toda expressly discloses that the process in Example 9 produces hollow particles with an inner hole diameter of 390 nm. A636, Table 2. This inner hole diameter was “observed and measured (photographic measurement).” A635[12:56-59]. Toda’s Table 2 also shows several other examples using potassium hydroxide to cause swelling in a base treatment step, which result in hollow polymer particles with an inner hole diameter observed using photographic measurement. A636, Table 2.

The patents-in-suit themselves recognize Toda’s express teaching of preparing voided polymer particles by swelling a core-shell polymer with a base swelling agent. The specification states, for example, that Toda produced “[v]oided latex particles . . . prepared by *swelling the core* of a core-shell emulsion polymer.” A32[1:39-45] (emphases added). The specification further states that Toda discloses “processes whereby, in the latter stages of polymerizing the shell, monomer is added to facilitate diffusion of base *into the core of the polymer in order to achieve swelling.*” A32[1:45-49] (emphasis added). The patents-in-suit thus confirm that Toda expressly discloses a “swelling agent.”

Based on Toda's extensive disclosure of using potassium hydroxide, which the patents-in-suit describe as a "[s]uitable swelling agent," to produce hollow polymer particles, the Board erred in finding that Toda does not expressly disclose a "swelling agent." Based on this express disclosure of a "swelling agent," the Board also erred in requiring Organik to establish the same limitation by inherency. Accordingly, the Board's decision that the '435 patent claims are not anticipated by Toda, and that the '004 patent claims would not have been obvious over Toda in view of Crouch, should be reversed.

**b. Touda Expressly Discloses Using Bases Such as Potassium Hydroxide or Sodium Hydroxide to Produce Hollow Polymer Particles**

Touda also discloses "a process for producing microvoid-containing polymer particles." A641[1:5-6]. Touda expressly discloses that a base, such as potassium hydroxide or sodium hydroxide, is used to achieve swelling and create the microvoids. A642[4:36-45]. It states, for example, that "the present inventors have found that if the polymer particles are swollen with a base in the presence of an organic solvent, microvoid-containing polymer particles can be obtained easily within a short period of time." A641[2:40-48]. Touda expressly discloses use of bases that the patents-in-suit define as swelling agents, including "alkali metal hydroxides such as sodium hydroxide, potassium hydroxide and lithium hydroxide." A642[4:36-45].

Similar to Toda, Touda teaches that the amount of the carboxyl-containing monomer is preferably between 0.1 to 40% of the total monomer to facilitate swelling and production of microvoids. A642[3:15-21] (“If the amount of the carboxyl-containing monomer is less than 0.1 part by weight, swelling of the copolymer particles with a base does not easily take place, and it is difficult to introduce microvoids into the copolymer.”). Touda further discloses that an organic solvent may be used to facilitate swelling of the polymer particles. A642[3:66-4:1] (“[A]ny organic solvent may be used which can fully swell the copolymer particles.”). Moreover, Touda teaches that the base should diffuse into the interior of the polymer particles. Touda states, for example, that, “[t]o neutralize the carboxyl groups inside the polymer particles with the base, time is required during which the base diffuses in the interiors of the latex particles.” A642[4:51-53].

As the Board recognized, Touda discloses examples in which the base swelling agent is added to the emulsion under conditions of no substantial polymerization. The Board cited Touda’s Examples 1A and 1B, which teach a process for producing “microvoid-containing latex” in which multi-stage emulsion polymer particles are first formed in an eight-hour process to complete polymerization. A20-21 (citing Touda, A643[6:51-67]). After polymerization is

completed, microvoids are formed by adding sodium hydroxide and solvent and stirring the mixture for three hours at 80°C. A21 (citing Touda, A644[7:4-24]).

Touda thus expressly discloses using sodium hydroxide or potassium hydroxide as a swelling agent to produce hollow polymer particles under conditions of no substantial polymerization of the monomer. Accordingly, the Board erred by finding that Touda does not expressly disclose a “swelling agent,” and further erred by requiring Organik to establish the same “swelling agent” limitation by inherency. The Board’s decision that the ’435 patent claims would not have been obvious over Touda should therefore be reversed.

### **3. The Board Erred by Relying on Dr. Schork’s Irrelevant Testimony and Faulty Testing**

It is undisputed that Toda and Touda disclose using potassium hydroxide, which the patents-in-suit describe as a suitable swelling agent. Nor is it disputed that Toda’s and Touda’s experimental results show that the disclosed processes produce hollow polymer particles with measurable microvoids, which Touda depicts with electron micrograph images. A639-40, Figs. 1(a)-1(c). The Board erred by ignoring these express disclosures based on testimony by Rohm and Haas’s expert, Dr. Schork, who questioned their “authenticity.” A2402-03, ¶ 108 (stating that his test results “call into question the authenticity of the entire [Toda] patent”).

Although the Board did not even address enablement, it nonetheless accepted Rohm and Haas's self-serving contention that the Toda and Touda references did not actually achieve the results they expressly disclose. In essence, the Board accepted Dr. Schork's opinion that both Toda and Touda were fraudulently procured based on falsified test results and photographs. There is no evidence that this is actually true, and the Board completely ignored the fact that issued U.S. patents are presumed enabled as a matter of statutory law. *See, e.g., Amgen Inc. v. Hoechst Marion Roussel, Inc.*, 314 F.3d 1313, 1355 (Fed. Cir. 2003) (holding that prior-art patents are presumed to be enabled for both their claimed and unclaimed disclosures); *see also* A15-16. Furthermore, for obviousness purposes, a reference does not need to be enabled; "it qualifies as a prior art, regardless, for whatever is disclosed therein." *Amgen*, 314 F.3d at 1357.

The Board's conclusions regarding Toda and Touda flow directly from its erroneous claim construction importing a swelling step into the claims and requiring that a "swelling agent" achieve swelling specifically by permeating the shell and swelling the core under conditions of no substantial polymerization, despite no such requirement being recited in the claims. The Board explained that its basis for discounting the express disclosure in Toda and Touda was Dr. Schork's testimony that a skilled artisan allegedly would have understood that potassium hydroxide would not have permeated the shell and swelled the core

under the specific process conditions in Toda and Touda. *See, e.g.*, A15 (citing Schork Decl., A2394-95, ¶¶ 92-93). This contention is irrelevant because, as discussed above, the claims-in-suit do not require swelling or any specific process conditions that facilitate swelling, and thus do not require swelling to occur in any specific fashion.

In the context of the prior art, all that is required is that a skilled artisan would understand that potassium hydroxide and the other bases disclosed in Toda and Touda would be capable of swelling the polymer particles under some suitable conditions, including subsequent processing conditions not recited in the claims. To this end, Dr. Schork himself testified that he interpreted the use of sodium hydroxide in Touda's Example 1B to be for the purpose of swelling the polymer particles. *See* A1018[58:1-11] ("If you want me to infer what they mean, I could infer that they were attempting to swell."). Dr. Schork further testified that Touda's experimental data disclose polymer particles with voids, and that a person of ordinary skill in the art would understand the reference to be reporting production of swollen polymer particles. *See, e.g.*, A1020[60:16-19] ("Q: Would a person of ordinary skill in the art understand that to be a swollen particle? A: Yes. That's what is reported here, swollen particle.>").

Similarly, with respect to Toda, Dr. Schork testified that a skilled artisan would understand the experimental data in Table 2 to be reporting a hollow particle



with a measureable inner hole diameter. *See* A1073-74[113:22-114:9] (“Q: Would a person of skill in the art reading table two understand that it is reporting a hollow particle that has a particle size of 450 nanometers, along with an inner hole of 390 nanometers? . . . A: One would understand that that is what’s being reported.”). Dr. Schork also testified that a skilled artisan would understand Table 2 in Toda as indicating that swelling occurred. *See* A1078-79[118:18-119:7] (“Q: From the written disclosure in [Toda], would a person of skill in the art have understood that the potassium hydroxide had a role in swelling the particles to create the particles that are reported in table two? . . . A: One would understand from table two that the patent is -- while not explicitly saying so, is showing you that swelling occurred.”). Dr. Schork thus testified that a skilled artisan would understand both Toda and Touda as teaching processes in which potassium hydroxide or sodium hydroxide are used to produce swollen polymer particles with measureable microvoids. The Board erred by ignoring Dr. Schork’s concessions that a skilled artisan would interpret Toda and Touda as teaching swelling.

After incorrectly finding that neither Toda nor Touda expressly disclosed a “swelling agent,” the Board relied on Dr. Schork’s experimental results in concluding that neither reference *inherently* discloses a swelling agent. A14-16 (citing Schork Decl., A2392-96, ¶¶ 89-94); A22-24 (citing Schork Decl., A2413-17, ¶¶ 139-51). Dr. Schork performed modified versions of the processes

disclosed in Toda and Touda and concluded that the potassium hydroxide and sodium hydroxide disclosed in those references would not permeate the polymer shell and swell the core. A15-16; A22-24; A71-72.

This testing is irrelevant because Organik was not required to show inherency where Toda and Touda expressly disclose the “swelling agent” limitation. Moreover, the Board improperly discounted testimony by Organik’s expert, Dr. Prud’homme, regarding flaws in Dr. Schork’s methodology. Dr. Prud’homme noted, for example, that Dr. Schork’s methodology differed from the process of Example 9 of Toda in numerous ways and resulted in a number of particles “three orders of magnitude more” than disclosed in Toda. A1202, ¶ 26; A1204-13, ¶¶ 31-46. Dr. Prud’homme also pointed out that, despite producing *one thousand times more particles than expected*, Dr. Schork did nothing to modify his methods to correct the error. A1203-04, ¶ 29. Dr. Prud’homme explained that having so many more particles would result in the particles being unstable, and concluded that it was unsurprising given this large difference that Dr. Schork’s attempt to replicate Toda’s Example 9 failed to yield the hollow polymer particles the Toda inventors produced. A1203, ¶ 27.

Dr. Schork similarly failed to faithfully replicate the processes disclosed in Touda, yet the Board again discounted Dr. Prud’homme’s testimony pointing out the errors in Dr. Schork’s methodology. A23-24. Notably, Dr. Prud’homme

pointed out that, when replicating Example 1B of Touda, Dr. Schork did not remove the solvent he had used, as disclosed in the reference itself. A1216-17, ¶ 54. Dr. Prud'homme explained that the solvent in Touda is used to soften the polymer particles so swelling can be accomplished at a lower temperature, and that Dr. Schork's failure to remove the solvent could have caused the particles to collapse on themselves, destroying any microvoids. A1217, ¶ 55.

Although the Board recognized the numerous inconsistencies between Dr. Schork's methods and results and those disclosed in Toda and Touda, it nonetheless relied on his testimony for the sole reason that Dr. Prud'homme had not provided contrary experimental data showing that Toda's and Touda's processes function as disclosed. A17-18; A24; A73. The Board stated:

Although we recognize Dr. Prud'homme's expertise in the field of emulsion polymerization, we do not accord his testimony, or Petitioner's arguments based on that testimony, persuasive weight. Dr. Prud'homme has not provided experimental data demonstrating that a different manner of performing the process of [Toda's] Example 9 would have provided results that differ from those observed in Dr. Schork's replications.

A17-18. The Board thus ignored the flaws in Dr. Schork's methodology based on the erroneous legal premise that Organik was required to prove through experimental testing that Toda and Touda inherently disclose what they already disclose expressly. Accordingly, the Board erred by demanding testing from

Dr. Prud'homme to prove inherency even though Toda and Touda *expressly* disclose providing or adding a “swelling agent” as properly construed.

## VII. CONCLUSION

For these reasons, this Court should reject the Board’s narrow construction of “swelling agent” and reverse its finding that claims 1-5 of the ’435 patent and claims 1-7 of the ’004 patent are not unpatentable.

Date: November 3, 2015

Respectfully submitted,

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## **ADDENDUM**

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Paper 56  
Entered: May 27, 2015

UNITED STATES PATENT AND TRADEMARK OFFICE

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BEFORE THE PATENT TRIAL AND APPEAL BOARD

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ORGANIK KIMYA AS,  
Petitioner,

v.

ROHM AND HAAS COMPANY,  
Patent Owner.

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Case IPR2014-00185  
Patent 6,020,435

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Before TONI R. SCHEINER, LORA M. GREEN, and  
ERICA A. FRANKLIN, *Administrative Patent Judges*.

FRANKLIN, *Administrative Patent Judge*.

FINAL WRITTEN DECISION  
*35 U.S.C. § 318(a) and 37 C.F.R. § 42.73*

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Patent 6,020,435

## I. INTRODUCTION

Organik Kimya AS (“Petitioner”) filed a Corrected Petition (Paper 10, “Pet.”) to institute an *inter partes* review of claims 1–5 of U.S. Patent No. 6,020,435 (Ex. 1001, “the ’435 patent”). Patent Owner, Rohm and Haas Company, did not file a Preliminary Response to the Petition.

In an Institution Decision (Paper 11, “Inst. Dec.”), an *inter partes* review of claims 1–5 was instituted. After the Institution Decision, Patent Owner filed a Response (Paper 30, “PO Resp.”) and a contingent Motion to Amend Claims (Paper 31, “Mot. Amend”). In response, Petitioner filed a Reply (Paper 36, “Pet. Reply”) and an Opposition to the Motion to Amend (Paper 37). Patent Owner then filed a Reply to Petitioner’s Opposition (Paper 45). Patent Owner also filed a Motion for Observations on Cross-Examination of Petitioner’s Reply Witness, Dr. Robert K. Prud’homme (Paper 48). Petitioner filed a Response to the Motion for Observations (Paper 50). The parties presented arguments at an oral hearing (Paper 55, “Tr.”).<sup>1</sup>

The Board has jurisdiction under 35 U.S.C. § 6(c). In this Final Written Decision, issued pursuant to 35 U.S. C. § 318(a) and 37 C.F.R. § 42.73, we determine Petitioner has not shown by a preponderance of the evidence that challenged claims 1–5 are unpatentable.

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<sup>1</sup> Petitioner and Patent Owner have filed Objections to Demonstrative Exhibits (Papers 53 and 54). In this Final Written Decision, we have not considered any arguments presented in the demonstrative exhibits that were not presented previously and/or are not supported by the record.

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*A. Related Matters*

According to Petitioner and Patent Owner, the '435 patent is involved in a case titled *Rohm and Haas Co. v. Organik Kimya San. Ve Tic. A.S.*, Case No. 13-cv-898-RGA, filed in the U.S. District Court for the District of Delaware, currently stayed; and in an investigation at the U.S. International Trade Commission titled *In the Matter of Certain Opaque Polymers*, Inv. No. 337-TA-883 (USITC). Pet. 2–3; Paper 9, 2–3 (Related Matters).

*B. The '435 Patent (Ex. 1001)*

The invention of the '435 patent is directed to a process for preparing multi-stage emulsion polymers having low dry-bulk density that are useful in coating compositions, such as paints and paper coatings. Ex. 1001, Abstract. Emulsion polymers, such as “hollow” or “voided” emulsion polymers, “are generally prepared by swelling a core/shell emulsion polymer in such a way that one or more voids form in the interior of the emulsion polymer particle. These voids contribute, among other things, to the opacity of coatings and films prepared with the hollow emulsion polymer.” *Id.* at 1:25–31. In some applications, it is desirable to minimize the weight of an applied coating. *Id.* at 1:32–33. “Accordingly, it is desirable to provide lightweight, low density additives for coatings, such as voided latex particles.” *Id.* at 1:37–38. The '435 patent explains that voided latex polymers are prepared by several known processes, such as by swelling the core of a core-shell emulsion polymer. *Id.* at 1:37–45. The '435 patent states:

The present invention seeks to overcome the deficiencies in the previously known processes by providing low density voided emulsion polymers and a process for preparing them.

*Id.* at 1:54–56.



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Specifically, the '435 patent discloses preparing the multi-stage emulsion polymer by sequential emulsion polymerization, which includes charging the monomers that form the shell. *Id.* at 7:29–31. “At, or near, the conclusion of charging the monomers which form the shell, the contents of the reactor include the multistage polymer, water and unreacted monomer.” *Id.* at 7:31–34. Under the conditions of emulsion polymerization, even if no additional monomer or initiator is added, there is an appreciable free-radical content in the system that keeps the polymerization process going until there is no longer an appreciable free-radical content. *Id.* at 7:34–39. When no appreciable free-radical content remains, no substantial amount of polymerization will occur. *Id.* at 7:39–42.

The '435 patent states: “We have discovered that by providing an aqueous emulsion of the multi-stage emulsion polymer, monomer and swelling agent under conditions wherein there is no substantial polymerization of the monomer, we can enhance the extent of swelling of the multistage emulsion polymer.” *Id.* at 7:56–60.

The '435 patent explains that suitable swelling agents may be volatile or fixed bases, or combinations thereof, and “include, are those which, in the presence of the multistage emulsion polymer and monomer are capable of permeating the shell and swelling the core.” *Id.* at 8:40–44.

### *C. Illustrative Claim*

Independent claim 1 of the '435 patent is illustrative of the claims at issue:

1. A process for preparing emulsion polymer particles comprising:
  - (a) providing an aqueous emulsion of
    - (i) multi-stage emulsion polymer, comprising a core stage polymer and a shell stage polymer, wherein the

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core stage polymer comprises, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core stage polymer, of hydrophilic monoethylenically unsaturated monomer, and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer; and wherein the shell stage polymer comprises, as polymerized units, at least 50 percent by weight of nonionic monoethylenically unsaturated monomer; (ii) monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer; and (iii) swelling agent under conditions wherein there is no substantial polymerization of the monomer; and (b) reducing the level of monomer by at least fifty percent.

*D. The Prior Art*

Toda et al., US 5,360,827, issued November 1, 1994 (Ex. 1003) (“Toda”).

Touda et al., US 5,077,320, issued December 31, 1991 (Ex. 1004) (“Touda”).

*E. The Instituted Grounds of Unpatentability*

Trial was instituted for Petitioner’s challenges to claims 1–5 of the ’435 patent on the following grounds:

Reference	Basis	’435 Claims Challenged
Toda	§ 102(b)	1–5
Touda	§ 103(a)	1–5

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## II. ANALYSIS

### A. Claim Construction

In an *inter partes* review, claim terms in an unexpired patent are interpreted according to their broadest reasonable constructions in light of the specification of the patent in which they appear. *See* 37 C.F.R. § 42.100(b); *In re Cuozzo Speed Techs., LLC*, 778 F.3d 1271, 1280 (Fed. Cir. 2015). Under the broadest reasonable construction standard, claim terms are presumed to be given their ordinary and customary meaning, as would be understood by one of ordinary skill in the art in the context of the entire disclosure. *In re Translogic Tech., Inc.*, 504 F.3d 1249, 1257 (Fed. Cir. 2007). An inventor may rebut that presumption by providing a definition of the term in the specification with reasonable clarity, deliberateness, and precision. *In re Paulsen*, 30 F.3d 1475, 1480 (Fed. Cir. 1994). Stated differently, a “claim term will not receive its ordinary meaning if the patentee acted as his own lexicographer and clearly set forth a definition of the disputed claim term in either the specification or prosecution history.” *CCS Fitness, Inc. v. Brunswick Corp.*, 288 F.3d 1359, 1366 (Fed. Cir. 2002).

The parties’ arguments center on the construction of the following claim term and phrase:

#### 1. “swelling agent”

Claim 1 requires the inclusion of a swelling agent in the aqueous emulsion. The Specification states,

Suitable swelling agents include, are those which, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core. Swelling agents may be aqueous or gaseous, volatile or fixed bases or combinations thereof.

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Suitable swelling agents include volatile bases such as ammonia, ammonium hydroxide, and volatile lower aliphatic amines, such as morpholine, trimethylamine, and triethylamine, and the like; fixed or permanent bases such as potassium hydroxide, lithium hydroxide, zinc ammonium complex, copper ammonium complex, silver ammonium complex, strontium hydroxide, barium hydroxide and the like.

Ex. 1001 at 8:40–52. The Specification explains,

The core polymer of the multistage emulsion polymer swells when the core is subjected to a basic swelling agent that permeates the shell to at least partially neutralize the hydrophilic-functionality of the core, preferably to a pH of at least about 6 to at least about 10, and thereby result in swelling by hydration of the hydrophilic core polymer.

*Id.* at 9:10–15.

Patent Owner asserts that that a person of ordinary skill in the art would understand from the Specification that the term “swelling agent” means

an ingredient that is capable of permeating the shell and swelling the core of the multi-stage emulsion polymer (ingredient (i) of step (a)) in the presence of the swelling monomer (ingredient (ii) of step (a)) under conditions of no substantial polymerization, in the process in which the ingredient in question is being employed as a “swelling agent.”

PO Resp. 21. For example, according to Patent Owner, sodium hydroxide, a fixed base, may be a swelling agent in some processes, while not in others.

*Id.* Patent Owner reasons that such a neutralizing agent “may or may not also be a ‘swelling agent’ depending on the conditions of the specific process where it is used.” *Id.* at 21–22. Patent Owner asserts, “[t]o contend that ‘swelling agent’ does not have to involve any amount of swelling ignores the functional aspects of the plain and ordinary meaning of term.”

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*Id.* at 27. Patent Owner’s position is supported by the Declaration of Patent Owner’s declarant, F. Joseph Schork, Ph.D. *See* Ex. 2011 ¶¶ 68–70.

Petitioner asserts that the claims do not require the recited “swelling agent” to be an ingredient that “‘must be capable of permeating the shell and swelling the core.’” Pet. Reply 3. Petitioner asserts that the Specification “merely identifies exemplary types of swelling agents” without defining or limiting the term. *Id.* at 4. In support of this assertion, Petitioner notes that the Specification uses the term “include” in its description of suitable swelling agents, i.e., “[s]uitable swelling agents *include*, are those which, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core.” Ex. 1001, 8:40–44 (emphasis added); Pet. Reply 4. According to Petitioner, by using the term “include,” the Specification “makes clear that swelling agents that are not capable of permeating the shell and swelling the core also fall within the scope of the invention.” Pet. Reply at 5. Petitioner asserts that Patent Owner’s proposed claim construction disregards the Specification’s use of the term “include” in an attempt “to completely change the meaning of the ‘435 patent’s disclosure” and to impart impermissibly a “swelling step” into claim 1. *Id.* at 4–5.

We disagree with Petitioner that the Specification’s use of the term “include,” when describing suitable swelling agents, “makes clear” that bases that are not capable of permeating the shell and swelling the core also fall within the scope of the invention. Rather, the Specification’s use of the word “include,” in this instance, is modified by the phrase immediately following it, i.e., “are those which,” suggesting that suitable swelling agents include only those which exhibit the functional characteristic thereafter

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described. *See* Ex. 1001, 8:40. In contrast, the following paragraph of the Specification describes the structural requirement for suitable swelling agents using the word “include,” without modifying it with a restrictive phrase. Instead, when disclosing the volatile, fixed and permanent bases, the word “include” is coupled with the phrases “such as” and “and the like,” signaling open-ended or inclusive categories of these bases. *See id.* at 8:45–52.

Further, we agree with Patent Owner that the Specification describes a swelling agent not merely as being capable of permeating a shell and swelling the core of a multistage emulsion polymer in the abstract, but specifically under the conditions of the specific process for which the agent is to be used. Indeed, the Specification explains that in its process for preparing emulsion polymers, the core polymer of the multistage emulsion polymer swells when it “is subjected to a basic swelling agent that permeates the shell to at least partially neutralize the hydrophilic-functionality of the core.” Ex. 1001, 9:10–15.

Based on the foregoing discussion, in light of the ’435 patent Specification, we construe the claim term “swelling agent” as expressing a structural element, i.e., “an aqueous or gaseous, volatile or fixed base, or combinations thereof,” in functional terms, i.e., “capable of permeating the shell and swelling the core, in the presence of the multistage polymer and monomer, under the conditions of the specific process for which the agent is to be used.” *See Greenberg v. Ethicon Endo-Surgery, Inc.*, 91 F.3d 1580, 1583 (Fed. Cir. 1996) (structural elements, e.g., “filter” and “brake,” may be expressed in functional terms).

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2. *“under conditions wherein there is no substantial polymerization of the monomer”*

Claim 1 requires the inclusion of a swelling agent in the aqueous emulsion “under conditions wherein there is no substantial polymerization of the monomer.” Although the Specification does not disclose a quantitative amount of polymerization that meets (or exceeds) the recited “no substantial polymerization” limitation, the Specification does disclose that “[t]here are many means for providing that no substantial polymerization of monomer is occurring.” Ex. 1001, 7:61–62. Those means include:

[T]he addition of one or more polymerization inhibitors, the addition of one or more reducing agents, waiting for a sufficient period of time until there are no longer an appreciable number of free-radicals by virtue of them terminating, cooling the contents of the reactor to limit the reactivity of the free-radicals, and combinations thereof.

*Id.* at 7:62–8:1.

In our Institution Decision, we interpreted the claim phrase “under conditions wherein there is no substantial polymerization of the monomer” as including, but not being limited to, conditions wherein one or more of these means specifically disclosed in the ’435 patent exist. Inst. Dec. 8.

Patent Owner “agrees with the construction adopted by the Board.” PO Resp. 18. However, Patent Owner asserts that “whatever means are used to achieve the required condition of ‘no substantial polymerization,’ a [person of ordinary skill in the art] would understand that those means must, in fact, create the stated condition.” *Id.* at 19. In other words, Patent Owner asserts that “under conditions wherein there is no substantial polymerization of the monomer” requires more than just the existence of one or more of the means for establishing this condition disclosed in the Specification. *Id.*

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Instead, according to Patent Owner, the claim phrase requires that the end result of implementing such means “must be to create a condition of ‘no substantial polymerization of the monomer.’” *Id.*

Petitioner asserts that Patent Owner’s proposed interpretation “produces an unworkable result,” as the Specification does not provide a quantitative way for determining whether the condition actually exists. Pet. Reply 6. However, as counsel for Patent Owner explained at the Oral Hearing, the Specification discusses no substantial polymerization existing when there is a depletion of free-radicals. *See* Tr. 41:11–22. Indeed, the Specification states, “[w]hen there is no appreciable free-radical content, in other words, when the radical flux is very low or approaches zero, then no substantial amount of polymerization will occur.” Ex. 1001, 7:39–42.

Accordingly, based on the foregoing discussion, in light of the ’435 patent Specification, we determine that the broadest reasonable interpretation of the claim phrase “under conditions wherein there is no substantial polymerization of the monomer” includes, but is not limited to, conditions wherein one or more of the means specifically disclosed in the ’435 patent exist, and/or wherein no appreciable free-radical content remains in the reactor including the multistage polymer and unreacted monomer.

*B. Anticipation by Toda*

Petitioner asserts that claims 1–5 are anticipated by Toda (Ex. 1003) under 35 U.S.C. § 102(b). Pet. 5, 20–34.

Toda discloses:

A process for preparation of latex of a hollow polymer which comprises adding a base, in the presence of a monomer, to latex containing carboxy-modified copolymer particles to make the pH of the latex 8 or more; adding a carboxyl group-containing



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monomer to make the pH of the latex 7 or less; and then polymerizing these monomers.

Ex. 1003, Abstract.

Toda discloses, in Example 9, a process for preparing hollow polymer particles comprising the steps of forming a center layer, an intermediate layer, and a surface layer. *Id.* at 11:59–68. The center layer is formed by placing in a reactor 400 parts of deionized water, 0.3 part of monomer mixture (a), i.e., 60% of methyl methacrylate (“MMA”), 5% of butyl acrylate (“BA”) and 35% of methacrylic acid (“MAA”), and 0.3 part of an emulsifier; heating the mixture to 80° C and stirring to prepare an emulsion; adding 7 parts of aqueous 3% potassium sulfate (“KPS”) solution; subjecting the mixture to polymerization at 80° C for 0.5 hour to obtain seed particles; adding 0.5 part of an emulsifier; continuously adding the residual monomer mixture (a) over a period of one hour; and carrying out polymerization for 2 hours, resulting in a conversion of monomer mixture (a) of 98%. *Id.* at 11:59–62, 12:13–26. An intermediate layer is formed by adding to the reactor 7 parts of KPS; continuously adding monomer mixture (b), i.e., 85% of MMA, 10% of BA and 5% of MAA; and carrying out polymerization for 4 hours, resulting in a conversion of mixture (b) of 98%. *Id.* at 11:63–66, 12:26–31. The surface layer is formed by adding 7 parts of KPS to the reactor; continuously adding monomer mixture (c), i.e., 95% of styrene and 5% of MMA; and carrying out polymerization for 4 hours, lowering the temperature to 20° C to obtain latex-containing polymer particles, wherein the conversion of monomer mixture (c) was 98%. *Id.* at 11:66–68, 12:31–37.

In particular, Toda discloses in Example 9 obtaining hollow polymer particles by (i) adding 3 parts of styrene to the obtained latex-containing

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polymer particles to soften the particles, and then adding 30 parts of aqueous 10% potassium hydroxide solution and heating to 80° C for 3 hours (base treatment); (ii) adding 80 parts of aqueous 5% MAA and 50 parts of styrene and stirring the mixture at 80° C for 3 hours (acid treatment); and (iii) adding 10 parts of aqueous 3% KPS solution, stirring the mixture of unreacted monomers at 80°C for 2 hours to carry out copolymerization, resulting in a polymerization conversion at this final stage of 99%. *Id.* at 12:38–59.

Petitioner asserts that Toda discloses, in at least Example 9, each and every element of claim 1 of the '435 patent. Pet. 22–26. We agree with Petitioner that Toda discloses in Example 9 that: (1) the core stage polymer (center layer polymer) comprises 35% of MAA, a hydrophilic monoethylenically unsaturated monomer, as well as 60% of MMA and 5% of BA, both of which are nonionic monoethylenically unsaturated monomers (*id.* at 22–23); (2) the shell stage polymer (surface layer) comprises 95% of styrene and 5% of MMA, both of which are nonionic monoethylenically unsaturated monomers (*id.* at 23, 29); and (3) a separate monomer comprised 3 parts of styrene, wherein the 3 parts was at least 0.5% by weight based on the weight of the multi-stage emulsion polymer (*id.* at 24).

However, based on our construction of the term “swelling agent,” and in consideration of the arguments and evidence, we disagree with Petitioner’s assertion that the process disclosed in Toda Example 9 includes adding a “swelling agent.” According to Petitioner, Toda’s addition of 30 parts of aqueous 10% potassium hydroxide solution to the reaction mixture meets this claim limitation. Pet. 24, 31. In the Petition, Petitioner supports this position by referring to Toda’s disclosure of adding potassium

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hydroxide solution in the process of Example 9 (Pet. 24 (citing Ex. 1003 at 12:40–43)), and to the testimony of Petitioner’s declarant, Dr. Marek W. Urban, who explains that potassium hydroxide “is a fixed base expressly identified by the ’435 patent as a possible swelling agent” (*id.* (citing Ex. 1002 ¶ 68)).

In the Response, Patent Owner asserts that Petitioner’s argument is based entirely on inherency, rather than any express disclosure by Toda that the potassium hydroxide used in Example 9 is a “swelling agent,” or is “capable of permeating the shell and swelling the core.” PO Resp. 36–37. Further, Patent Owner asserts that Petitioner has not established that such inherency exists by providing, for example, data or experimental evidence that the potassium hydroxide used in Toda’s Example 9 is capable of permeating the shell and swelling the core of the multi-stage emulsion polymer “*each and every time.*” *Id.* at 37–38.

In the Reply, Petitioner argues that Toda discloses a “swelling agent” expressly, not inherently, by disclosing potassium hydroxide in Example 9. Pet. Reply 7.

We disagree with Petitioner. We have construed the claim term “swelling agent” as encompassing a structure, i.e., a base, and a function, i.e., being capable of permeating the shell and swelling the core, in the presence of the multistage polymer and monomer, under the conditions of the specific process for which the agent is to be used. Petitioner has neither asserted nor shown that Toda *expressly* teaches that potassium hydroxide permeates the shell and swells the core of the multi-stage polymer in Toda’s Example 9. Instead, Petitioner asserts that potassium hydroxide permeates the shell and swells the core of the polymer particles in Toda because the

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same polymer particles are described in the '435 patent as suitable for swelling. Pet. Reply 14 (citing Ex. 1002 ¶¶ 62–66). In other words, Petitioner's argument is that Toda *inherently* discloses that potassium hydroxide is capable of permeating the shell and swelling the core of the polymer particles in Toda's Example 9.

With respect to Petitioner's inherency argument, what is missing is some consideration of the reaction conditions in the process of Toda's Example 9. In Toda's Example 9, the potassium hydroxide was added to the mixture after the temperature of the mixture was lowered to 20° C and styrene was added to soften the polymer particles. Ex. 1003, 12:35–42. Patent Owner provides persuasive evidence, through the Declaration of Dr. Schork, that a person of ordinary skill in the art would have understood that the shell would be too hard at this temperature for potassium hydroxide to be capable of permeating the shell and swelling the core. PO Resp. 39 (citing Ex. 2011 ¶ 92). Petitioner has not argued persuasively otherwise. *See, e.g.*, Pet. Reply 13–14.

Further, in Toda's Example 9, after adding the potassium hydroxide, the mixture is heated to 80 °C. Ex. 1003, 12:41–44. Patent Owner provides persuasive evidence, also through the Declaration of Dr. Schork, that, based on the teachings of Toda, a person of ordinary skill in the art would not expect potassium hydroxide to permeate the shell and swell the core at that temperature either. PO Resp. 39 (citing Ex. 2011 ¶¶ 86, 92); *see also* Ex. 2011 ¶ 93 (explaining why a person of ordinary skill would not consider potassium hydroxide a “swelling agent” when the reaction temperature of Toda Example 9 is increased to 80 °C). Here again, Petitioner has not argued persuasively otherwise. *See, e.g.*, Pet. Reply 13–14.

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Additionally, Patent Owner provides persuasive experimental evidence that the potassium hydroxide solution used in Toda's Example 9 is not capable of permeating the shell and swelling the core. *See* PO Resp. 38. Dr. Schork attempted to replicate Toda's Example 9 twice and observed each time that potassium hydroxide was not capable of permeating the shell and swelling the core of the multi-stage emulsion polymer. Ex. 2011 ¶¶ 89–94). According to Dr. Schork, results of those replications did not provide any swelling during the base treatment of Example 9, suggesting that potassium hydroxide did not perform as a swelling agent under the conditions of Toda's Example 9, as required by claims 1–5 of the '435 patent. *See id.* ¶¶ 94, 102–103.

Petitioner challenges the probative value of Dr. Schork's experimental data by asserting that Dr. Schork "only tried to reproduce Example 9 of Toda twice," and that he did not "adequately replicate" the process. Pet. Reply 12. More specifically, Petitioner asserts that Dr. Schork did not accurately replicate Example 9 of Toda because: (1) his reaction produced almost a thousand times more particles than a person of ordinary skill in the art would expect; and (2) he used a different device to add the KPS to the reaction mixture. In support of these assertions, Petitioner relies on the Declaration of Petitioner's declarant, Dr. Robert K. Prud'homme (Ex. 1021). Pet. Reply 12 (citing Ex. 1021 ¶¶ 26, 41).

According to Dr. Prud'homme, "if a skilled artisan trying to replicate Example 9 does not achieve the estimated number of particles or required particle size, he would readily understand what factors to adjust to reproduce Example 9." Ex. 1021 ¶ 29. Dr. Prud'homme acknowledged that Dr. Schork disagreed with this opinion. *See id.* (citing Ex. 1020, 135 (Schork

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Deposition)).

Further, in Dr. Prud'homme's opinion, Dr. Schork's use of a sub-surfacing metering device to add the KPS to the reaction mixture, instead of using a separating funnel as described in Toda's Example 9, led to a more uniform addition than in Toda, and resulted in a higher overall nucleation. *Id.* ¶ 41. According to Dr. Prud'homme, "[a] less uniform addition, like the one that would occur with a separatory funnel, would lead to 'bursts' of radical initiation. Such bursts may lead to radical termination, which leads to decreased numbers of particles." *Id.* ¶ 40. Additionally, Petitioner asserts, and Dr. Prud'homme explains, that Dr. Schork's elimination of all of the oxygen from the reaction increased the nucleation rate. Pet. Reply 13 (citing Ex. 1020 ¶ 34).

Petitioner asserts also that "Dr. Schork may have used almost four times the amount of emulsifier than what a skilled artisan would have used given the number of particles he obtained when attempting to replicate Example 9 of *Toda*." Pet. Reply 13 (citing Ex. 1021 ¶¶ 38–39). However, in his Declaration, Dr. Prud'homme states that Dr. Schork's approach was "not unreasonable." Ex. 1021 ¶ 39. Dr. Prud'homme merely offered a different approach which would have resulted in using less emulsifier, stating, "it is also entirely reasonable to read Example 9 to mean 0.3 parts of a 23% solution of SDBS." *Id.*

Although we recognize Dr. Prud'homme's expertise in the field of emulsion polymerization, we do not accord his testimony, or Petitioner's arguments based on that testimony, persuasive weight. Dr. Prud'homme has not provided experimental data demonstrating that a different manner of performing the process of Example 9 would have provided results that differ

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from those observed in Dr. Schork's replications. Nor has the Petitioner provided any experimental data or evidence establishing that the process of Toda's Example 9 inherently disclosed a "swelling agent," as required by claims 1–5 of the '435 patent. *See MEHL/Biophile Int'l. Corp. v. Milgraum*, 192 F.3d 1362, 1365 (Fed. Cir. 1999) (quoting *In re Oelrich*, 666 F.2d 578, 581 (CCPA 1981)) ("Inherency . . . may not be established by probabilities or possibilities. The mere fact that a certain thing *may* result from a given set of circumstances is not sufficient."); *see also Glaxo Inc. v. Novopharm Ltd.*, 52 F.3d 1043, 1047 (Fed. Cir. 1995) (inherency precluded where patentee's chemist twice produced different crystals from the same method).

Accordingly, after considering the arguments and evidence, and based upon our construction of the term "swelling agent," we find that Petitioner has not shown that Toda discloses potassium hydroxide as a "swelling agent" in the process of Example 9.

Based on the foregoing discussion and the record, we conclude that Petitioner has not shown by a preponderance of the evidence that Toda anticipates claims 1–5. *See In re Schreiber*, 128 F.3d 1473, 1477 (Fed. Cir. 1997) ("To anticipate a claim, a prior art reference must disclose every limitation of the claimed invention, either explicitly or inherently.").

### *C. Obviousness over Touda*

Petitioner contends that claims 1–5 would have been obvious over Touda (Ex. 1004) under 35 U.S.C. § 103(a). Pet. 5, 34–47. Touda discloses:

A process for producing polymer particles containing one microvoid or two or more discrete microvoids, which comprises (1) adding a base to a latex of a carboxyl-modified copolymer containing 0.1 to 1000 parts of an organic solvent per 100 parts by weight of the carboxyl-modified copolymer to neutralize at

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least part of the carboxyl groups in the copolymer, and (2) adding an acid to the latex to adjust the pH of the latex to not more than 7.

Ex. 1004, Abstract. Touda explains that:

[T]he present inventors have found that if the polymer particles are swollen with a base in the presence of an organic solvent, microvoid-containing polymer particles can be obtained easily with a short period of time, and microvoid-containing particles of a polymer having a high glass transition temperature can be obtained, and that this process can also give polymer particles having a plurality of microvoids.

*Id.* at 2:41–48.

Further, Touda teaches that “[t]here is no particular limitation on the method of obtaining polymers containing carboxyl groups,” and discloses that the method may include copolymerizing carboxyl-containing monomers, which “is advantageous to production.” *Id.* at 2:66–3:4. Touda discloses that exemplary carboxyl-containing monomers that can be used in the invention include ethylenically unsaturated carboxylic acids, such as methacrylic acid, and that exemplary monomers, which are copolymerizable with carboxyl-containing monomers, include aromatic vinyl monomers, such as styrene. *Id.* at 3:5–8, 25–29.

Additionally, Touda teaches that “[t]here is no particular restriction on the method of including an organic solvent in the carboxyl-modified copolymer latex,” and the method may, for example, involve adding an organic solvent to a latex obtained by polymerization. *Id.* at 3:61–64. The organic solvent used in the invention also is not particularly limited, as long as it “can fully swell the copolymer particles.” *Id.* at 3:66–4:1. Touda discloses specific examples of solvents, including toluene. *Id.* at 4:1–3.

“When an organic solvent is added to the latex after preparation of the latex



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of the carboxyl-modified copolymer, at least one of polymerizable organic solvent may be used . . . such as styrene . . . .” *Id.* at 4:16–21.

Petitioner asserts that Touda discloses each and every element of claim 1 of the ’435 patent. Pet. 35. According to Petitioner, “*Touda* expressly discloses all but one of the elements of claim 1 of the ’435 patent in a single example – Example 1 (combination of Examples 1S, 1A and 1B).” *Id.* at 36 (citing Ex. 1002 ¶ 80). Petitioner asserts that the one element not disclosed in Touda Example 1 is taught expressly elsewhere in the disclosure of Touda. *Id.*

Touda discloses in Example 1S the “[s]ynthesis of a seed latex,” comprising: placing 300 parts of deionized water in a reactor, along with 95 parts of styrene (i.e., 95% of a nonionic monoethylenically unsaturated monomer), and 5 parts of MAA (i.e., 5% of a hydrophilic monoethylenically unsaturated monomer); heating and stirring the mixture; allowing the temperature of the mixture to reach 70° C and then adding 17 parts of a 3% aqueous solution of potassium persulfate; and maintaining the reaction mixture at 70° C for three hours to complete the polymerization reaction, resulting in a polymerization conversion of 99%. Ex. 1004, 6:33–49; Pet. 36.

Touda discloses in Example 1A the “[p]roduction of a filled polymer latex,” comprising: charging the same reactor used in the production of the seed latex with 518 parts of deionized water and 3.4 parts of seed latex; allowing the temperature of the reactor to reach 80° C and then adding 30 parts of a 3% aqueous solution of potassium persulfate; adding a monomeric mixture composed of 94 parts of styrene (i.e., at least 50% by weight of nonionic monoethylenically unsaturated monomer), and 6 parts of acrylic

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acid over the course of 6 hours; maintaining the reaction mixture at 80° C for two hours to complete polymerization, resulting in a polymerization conversion of 97%. Ex. 1004, 6:51–67.

In particular, Touda discloses in Example 1B the “[p]roduction of a microvoid-containing latex,” comprising: charging the same reactor used in the production of the seed latex with 870 parts of deionized water, 100 parts of the filled polymer latex, 1 part of sodium dodecyl-benzenesulfate, 30 parts of toluene, and 33 parts of a 10% aqueous solution of sodium hydroxide (“NaOH”); stirring the mixture at 80° C for three hours; adding 300 parts of a 1% aqueous solution of hydrochloric acid; stirring the mixture at 80° C for 3 hours; cooling the reaction mixture to room temperature; and removing the organic solvent under reduced pressure. *Id.* at 7:4–24; Pet. 37.

Petitioner asserts that it would have been obvious to a person of ordinary skill in the art at the time the invention was made to have modified the process of Touda’s Example 1 by substituting styrene, a polymerizable organic solvent, in place of the organic solvent toluene. Petitioner reasons that the artisan would have been motivated to make this modification because Touda teaches that a polymerizable organic solvent, such as styrene, may be used when the organic solvent is added to the latex after preparation of the latex of the carboxyl-modified copolymer (*id.* at 4:16–21), as in the process of Example 1B (*see id.* at 7:6–10).

Patent Owner argues, among other things, that Touda does not disclose expressly all but one of the elements of claim 1 of the ’435 patent in Example 1. PO Resp. 50. In particular, Patent Owner asserts that Touda does not disclose expressly sodium hydroxide, or any other base, as a

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“swelling agent,” i.e., being capable of permeating the shell and swelling the core of the emulsion polymer under the conditions of Example 1. *Id.*

In the Reply, Petitioner asserts that Touda discloses a “swelling agent” expressly, not inherently, by disclosing sodium hydroxide in Example 1. Pet. Reply 7.

In view of our construction of the claim term “swelling agent,” we disagree with Petitioner. As discussed previously, we have construed the claim term “swelling agent” as encompassing a structure, i.e., a base, and a function, i.e., being capable of permeating the shell and swelling the core, in the presence of the multistage polymer and monomer, under the conditions of the specific process for which the agent is to be used. Petitioner has neither asserted nor shown that Touda *expressly* teaches that sodium hydroxide permeates the shell and swells the core of the multi-stage polymer in Touda’s Example 1. Nor has Petitioner asserted or shown that Touda *suggests* that sodium hydroxide is capable of functioning in this manner. Instead, Petitioner asserts that sodium hydroxide permeates the shell and swells the core of the polymer particles in Touda because the same polymer particles are described in the ’435 patent as suitable for swelling. Pet. Reply 14 (citing Ex. 1002 ¶¶ 85–88). In other words, Petitioner’s argument is that Touda *inherently* discloses that sodium hydroxide is capable of permeating the shell and swelling the core of the polymer particles in Touda’s Example 1.

With respect to Petitioner’s argument, Patent Owner asserts that a person of ordinary skill in the art would understand that the sodium hydroxide used in Example 1 is not capable of permeating the shell and swelling the core of the emulsion polymer under the conditions described in

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Example 1. PO Resp. 50. In support of this assertion, Patent Owner relies on the Declaration of Patent Owner's declarant, Dr. Schork. *Id.* (citing Ex. 2011 ¶¶ 127–128). Dr. Schork explains that in Touda's Example 1, the core is only 5 parts (5%) methacrylic acid and the shell is only 6 parts (6%) acrylic acid, such that the core and the shell are only slightly acidic. Ex. 2011 ¶ 128. Dr. Schork states that a person of skill in the art “would understand that under these conditions, NaOH would at best neutralize the shell, not the core.” *Id.* According to Dr. Schork, “[g]iven the low levels of acid, the NaOH would be unlikely to permeate and neutralize any part of the particle. Certainly, NaOH would not permeate the shell and swell the core. Instead, to the extent that any swelling occurred, it would take place in the shell.” *Id.*

Additionally, Patent Owner provides persuasive experimental evidence that the sodium hydroxide solution used in Touda's Example 9 was not capable of permeating the shell and swelling the core. *See* PO Resp. 51. Dr. Schork replicated the process of Touda's Example 1. *Id.* (citing Ex. 2011 ¶¶ 139–151). According to Dr. Schork, his experiment resulted in “no observable swelling occurred during the reported ‘swelling stage’” (Ex. 2011 ¶ 151), or any polymer particles with voids, which “demonstrates that the NaOH used in Example 1 is not capable of permeating the shell and swelling the core of the emulsion under the conditions described therein” (*id.* ¶ 130).

Petitioner challenges the probative value of Dr. Schork's experimental data by asserting that he “only tried to reproduce Example 1 of [Touda] twice,” and that he did not “adequately replicate” the process. Pet. Reply 12. However, Petitioner has not explained how Dr. Schork's experiment did not

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adequately replicate Touda's Example 1. *See* Pet. Reply 12. Nor has Petitioner provided any experimental data demonstrating that a different manner of performing the process would have provided results that differ from those observed from Dr. Schork's experiment. Indeed, Petitioner has not provided any experimental evidence contradicting Dr. Schork's results or supporting its position that Touda uses a "swelling agent," as required by claims 1–5 of the '435 patent.

Accordingly, after considering the arguments and evidence, and based upon our construction of the term "swelling agent," we find that Petitioner has not established that Touda teaches or suggests the invention of claims 1–5 of the '435 patent.

Based on the foregoing discussion and the record, we conclude that Petitioner has not shown by a preponderance of the evidence that claims 1–5 would have been obvious over Touda under 35 U.S.C. § 103(a).

### III. MOTION TO AMEND

Patent Owner's Motion to Amend is contingent on claims 1–5 of the '435 patent being held unpatentable. Mot. Amend 2. Because these claims are not held to be unpatentable, there is no occasion to reach or decide the motion to amend.

### IV. CONCLUSION

Petitioner has not demonstrated by a preponderance of the evidence that claims 1–5 instituted for *inter partes* review are unpatentable under 35 U.S.C. § 102(b) as anticipated by Toda, or under 35 U.S.C. § 103(a) as obvious over Touda.

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ORDER

In consideration of the foregoing, it is hereby:

ORDERED that Petitioner's request for cancellation of claims 1–5 of the '435 patent is *denied*;

FURTHER ORDERED that Patent Owner's Motion to Amend is *dismissed* as moot; and

FURTHER ORDERED that, because this is a Final Written Decision, parties to the proceeding seeking judicial review of the decision must comply with the notice and service requirements of 37 C.F.R. § 90.2.

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Paper 40

Entered: June 26, 2015

UNITED STATES PATENT AND TRADEMARK OFFICE

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BEFORE THE PATENT TRIAL AND APPEAL BOARD

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ORGANIK KIMYA AS,  
Petitioner,

v.

ROHM AND HAAS COMPANY,  
Patent Owner.

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Case IPR2014-00350  
Patent 6,252,004 B1

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Before TONI R. SCHEINER, LORA M. GREEN, and  
ERICA A. FRANKLIN, *Administrative Patent Judges*.

FRANKLIN, *Administrative Patent Judge*.

FINAL WRITTEN DECISION  
*35 U.S.C. § 318(a) and 37 C.F.R. § 42.73*

Case IPR2014-00350  
Patent 6,252,004 B1

## I. INTRODUCTION

Organik Kimya AS (“Petitioner”) filed a Petition (Paper 2, “Pet.”) to institute an *inter partes* review of claims 1–7 of U.S. Patent No. 6,252,004 B1 (Ex. 1001, “the ’004 patent”). Patent Owner, Rohm and Haas Company, did not file a Preliminary Response to the Petition.

In an Institution Decision (Paper 9, “Inst. Dec.”), an *inter partes* review of claims 1–7 was instituted. After the Institution Decision, Patent Owner filed a Response (Paper 22, “PO Resp.”) and a contingent Motion to Amend Claims (Paper 23, “Mot. Amend”). In response, Petitioner filed a Reply (Paper 27, “Pet. Reply”) and an Opposition to the Motion to Amend (Paper 28). Patent Owner then filed a Reply to Petitioner’s Opposition (Paper 31). The parties presented arguments at an oral hearing (Paper 39, “Tr.”).<sup>1</sup>

The Board has jurisdiction under 35 U.S.C. § 6(c). In this Final Written Decision, issued pursuant to 35 U.S. C. § 318(a) and 37 C.F.R. § 42.73, we determine Petitioner has not shown by a preponderance of the evidence that challenged claims 1–7 are unpatentable.

### A. Related Matters

According to Petitioner and Patent Owner, the ’004 patent is involved in a case titled *Rohm and Haas Co. v. Organik Kimya San. Ve Tic. A.S.*, Case No. 13-cv-898-RGA, filed in the U.S. District Court for the District of Delaware, currently stayed; and in an investigation at the U.S. International

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<sup>1</sup> Petitioner and Patent Owner have filed Objections to Demonstrative Exhibits (Papers 37 and 38). In this Final Written Decision, we have not considered any arguments presented in the demonstrative exhibits that were not presented previously and/or are not supported by the record.



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Trade Commission titled *In the Matter of Certain Opaque Polymers*, Inv. No. 337-TA-883 (USITC). Pet. 2–3; Paper 8, 2–3 (Related Matters).

*B. The '004 Patent (Ex. 1001)*

The '004 patent is directed to a process for preparing multi-stage emulsion polymers having low dry-bulk density that are useful in coating compositions, such as paints and paper coatings. Ex. 1001, Abstract. Emulsion polymers, such as “hollow” or “voided” emulsion polymers, “are generally prepared by swelling a core/shell emulsion polymer in such a way that one or more voids form in the interior of the emulsion polymer particle. These voids contribute, among other things, to the opacity of coatings and films prepared with the hollow emulsion polymer.” *Id.* at 1:27–33. In some applications, it is desirable to minimize the weight of an applied coating. *Id.* at 1:34–35. “Accordingly, it is desirable to provide lightweight, low density additives for coatings, such as voided latex particles.” *Id.* at 1:39–40. The '004 patent explains that voided latex polymers are prepared by several known processes, such as by swelling the core of a core-shell emulsion polymer. *Id.* at 1:37–45. The '004 patent states:

The present invention seeks to overcome the deficiencies in the previously known processes by providing low density voided emulsion polymers and a process for preparing them.

*Id.* at 1:56–58.

Specifically, the '004 patent discloses preparing the multi-stage emulsion polymer by sequential emulsion polymerization, which includes charging the monomers which form the shell. *Id.* at 7:33–35. “At, or near, the conclusion of charging the monomers which form the shell, the contents of the reactor include the multistage polymer, water and unreacted monomer.” *Id.* at 7:35–38. Under the conditions of emulsion

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polymerization, even if no additional monomer or initiator is added, there is an appreciable free-radical content in the system that keeps the polymerization process going until there is no longer an appreciable free-radical content. *Id.* at 7:38–43. When no appreciable free-radical content remains, no substantial amount of polymerization will occur. *Id.* at 7:43–46.

The '004 patent states: “We have discovered that by providing an aqueous emulsion of the multi-stage emulsion polymer, monomer and swelling agent under conditions wherein there is no substantial polymerization of the monomer, we can enhance the extent of swelling of the multistage emulsion polymer.” *Id.* at 7:60–64.

The '004 patent explains that suitable swelling agents may be volatile or fixed bases, or combinations thereof, and “include, are those which, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core.” *Id.* at 8:43–46.

### *C. Illustrative Claim*

Independent claim 1 of the '004 patent is illustrative of the claims at issue:

1. A process for preparing emulsion polymer particles comprising:
  - (a) providing an aqueous emulsion of
    - (i) multi-stage emulsion polymer, comprising a core stage polymer and a shell stage polymer, wherein the core stage polymer comprises, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core stage polymer, of hydrophilic monoethylenically unsaturated monomer, and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer; and

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wherein the shell stage polymer comprises, as polymerized units, at least 50 percent by weight of nonionic monoethylenically unsaturated monomer;

(b) adding an effective amount of one or more polymerization inhibitors or reducing agents to substantially stop any polymerization;

(c) providing monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer;

(d) adding swelling agent; and

(e) reducing the level of monomer by at least fifty percent.

Ex. 1001, 37:14–38:5.

#### *D. The Prior Art*

Touda et al., US 5,077,320, issued December 31, 1991 (Ex. 1003) (“Touda”).

Toda et al., US 5,360,827, issued November 1, 1994 (Ex. 1004) (“Toda”).

Overbeek et al., US 5,292,660, issued March 8, 1994 (Ex. 1005) (“Overbeek”).

Crouch, US 2,574,020, issued November 6, 1951 (Ex. 1006) (“Crouch”).

#### *E. The Instituted Grounds of Unpatentability*

Trial was instituted for Petitioner’s challenges claims 1–7 of the ’004 patent on the following grounds:

Reference	Basis	’004 Claims Challenged
Touda	§ 103(a)	1–6
Touda and Overbeek	§ 103(a)	7
Toda and Crouch	§ 103(a)	1–7

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## II. ANALYSIS

### A. Claim Construction

In an *inter partes* review, claim terms in an unexpired patent are interpreted according to their broadest reasonable constructions in light of the specification of the patent in which they appear. *See* 37 C.F.R. § 42.100(b); *In re Cuozzo Speed Techs., LLC*, 778 F.3d 1271, 1280 (Fed. Cir. 2015). Under the broadest reasonable construction standard, claim terms are presumed to be given their ordinary and customary meaning, as would be understood by one of ordinary skill in the art in the context of the entire disclosure. *In re Translogic Tech., Inc.*, 504 F.3d 1249, 1257 (Fed. Cir. 2007). An inventor may rebut that presumption by providing a definition of the term in the specification with reasonable clarity, deliberateness, and precision. *In re Paulsen*, 30 F.3d 1475, 1480 (Fed. Cir. 1994). Stated differently, a “claim term will not receive its ordinary meaning if the patentee acted as his own lexicographer and clearly set forth a definition of the disputed claim term in either the specification or prosecution history.” *CCS Fitness, Inc. v. Brunswick Corp.*, 288 F.3d 1359, 1366 (Fed. Cir. 2002).

The parties’ arguments center on the construction of the following claim term and phrase:

#### 1. “swelling agent”

Claim 1 requires the inclusion of a swelling agent in the aqueous emulsion. The Specification states,

Suitable swelling agents include, are those which, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core. Swelling agents may be aqueous or gaseous, volatile or fixed bases or combinations thereof.

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Suitable swelling agents include volatile bases such as ammonia, ammonium hydroxide, and volatile lower aliphatic amines, such as morpholine, trimethylamine, and triethylamine, and the like; fixed or permanent bases such as potassium hydroxide, lithium hydroxide, zinc ammonium complex, copper ammonium complex, silver ammonium complex, strontium hydroxide, barium hydroxide and the like.

Ex. 1001 at 8:44–56. The Specification explains,

The core polymer of the multistage emulsion polymer swells when the core is subjected to a basic swelling agent that permeates the shell to at least partially neutralize the hydrophilic-functionality of the core, preferably to a pH of at least about 6 to at least about 10, and thereby result in swelling by hydration of the hydrophilic core polymer.

*Id.* at 9:14–19.

Patent Owner asserts that that a person of ordinary skill in the art would understand from the Specification that the term “swelling agent” means

an ingredient that is capable of permeating the shell and swelling the core of the multi-stage emulsion polymer (step (a)) in the presence of the swelling monomer (step (c)) under conditions of no substantial polymerization (step (b)), in the process in which the ingredient in question is being employed as a “swelling agent.”

PO Resp. 19–20. For example, according to Patent Owner, sodium hydroxide, a fixed base, may be a swelling agent in some processes, while not in others. *Id.* at 20. Patent Owner reasons that such a neutralizing agent “may or may not also be a ‘swelling agent’ depending on the conditions of the specific process where it is used.” *Id.* Patent Owner asserts, “[t]o contend that ‘swelling agent’ does not have to involve any amount of swelling ignores the functional aspects of the plain and ordinary meaning of

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term.” *Id.* at 24. Patent Owner’s position is supported by the Declaration of Patent Owner’s Declarant, F. Joseph Schork, Ph.D. *See* Ex. 2005 ¶¶ 67–69.

Petitioner asserts that the claims do not require the recited “swelling agent” to be an ingredient that “‘must be capable of permeating the shell and swelling the core.’” Pet. Reply 4. Petitioner asserts that the Specification “merely identifies exemplary types of swelling agents” without defining or limiting the term. *Id.* at 5. In support of this assertion, Petitioner notes that the Specification uses the term “include” in its description of suitable swelling agents, i.e., “[s]uitable swelling agents *include*, are those which, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core,” Ex. 1001, 8:44–46 (emphasis added). Pet. Reply 5. According to Petitioner, by using the term “include,” the Specification “mak[es] clear that swelling agents that are not capable of permeating the shell and swelling the core also fall within the scope of the invention.” *Id.* at 6. Petitioner asserts that Patent Owner’s proposed claim construction disregards the Specification’s use of the term “include” in an attempt “to change the meaning of the ‘004 patent disclosure” and to impart impermissibly a “swelling step” into claim 1. *Id.*

We disagree with Petitioner that the Specification’s use of the term “include,” when describing suitable swelling agents, “mak[es] clear” that bases that are not capable of permeating the shell and swelling the core also fall within the scope of the invention. *Id.* Rather, the Specification’s use of the word “include,” in this instance, is modified by the phrase immediately following it, i.e., “are those which,” suggesting that suitable swelling agents include only those which exhibit the functional characteristic thereafter described. *See* Ex. 1001, 8:44. In contrast, the subsequent paragraph of the

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Specification describes the structural requirement for suitable swelling agents using the word “include,” without modifying it with a restrictive phrase. Instead, when disclosing the volatile, fixed and permanent bases, the word “include” is coupled with the phrases “such as” and “and the like,” signaling open-ended or inclusive categories of these bases. *See id.* at 8:49–56.

Further, we agree with Patent Owner that the Specification describes a swelling agent not merely as being capable of permeating a shell and swelling the core of a multistage emulsion polymer in the abstract, but specifically under the conditions of the specific process for which the agent is to be used. Indeed, the Specification explains that in its process for preparing emulsion polymers, the core polymer of the multistage emulsion polymer swells when it “is subjected to a basic swelling agent that permeates the shell to at least partially neutralize the hydrophilic-functionality of the core.” Ex. 1001, 9:14–17.

Based on the foregoing discussion, in light of the ’004 patent Specification, we construe the claim term “swelling agent” as expressing a structural element, i.e., “an aqueous or gaseous, volatile or fixed base, or combinations thereof,” in functional terms, i.e., “capable of permeating the shell and swelling the core, in the presence of the multistage polymer and monomer, under the conditions of the specific process for which the agent is to be used.” *See Greenberg v. Ethicon Endo-Surgery, Inc.*, 91 F.3d 1580, 1583 (Fed. Cir. 1996) (structural elements, e.g., “filter” and “brake,” may be expressed in functional terms).

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2. “*adding an effective amount of one or more polymerization inhibitors or reducing agents to substantially stop any polymerization*”

Claim 1 requires “adding an effective amount of one or more polymerization inhibitors or reducing agents to substantially stop any polymerization.” The Specification states that “[w]hen used, the polymerization inhibitors or reducing agents are added in effective amount to substantially stop any polymerization, *generally from 25 to 5,000 parts per million (‘ppm’), preferably from 50 to 3,500 ppm based on polymer solids.*” Ex. 1001, 8:16–20 (emphasis added).

In our Institution Decision we interpreted the claim phrase “adding an effective amount of one or more polymerization inhibitors or reducing agents to substantially stop any polymerization,” as including, but not being limited to, adding an amount of polymerization inhibitors or reducing agents generally from 25 to 5,000 ppm, preferably from 50 to 3,500 ppm based on polymer solids, or in amounts exceeding these ranges. Inst. Dec. 7.

Patent Owner asserts “‘an effective amount’ to ‘substantially stop polymerization’ . . . depends entirely on the specific inhibitor or reducing agent and the specific reaction conditions of the process, including the starting amount of monomer and residual initiator.” PO Resp. 18. Therefore, according to Patent Owner, the claim phrase “adding an effective amount of one or more polymerization inhibitors or reducing agents to substantially stop any polymerization,” is not satisfied unless polymerization is substantially stopped as a result of adding the inhibitor or reducing agent used. *Id.* at 17.

Petitioner asserts that Patent Owner’s proposed interpretation “produces an unworkable result,” as the Specification does not provide a



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quantitative way for determining whether the condition actually exists. Pet. Reply 9. However, the Specification explains that no substantial polymerization exists when there is a depletion of free-radicals. *See* Ex. 1001, 7:43–46 (“When there is no appreciable free-radical content, in other words, when the radical flux is very low or approaches zero, then no substantial amount of polymerization will occur.”).

Accordingly, based on the foregoing discussion, in light of the ’004 patent Specification, we determine that the broadest reasonable interpretation of the claim phrase “adding an effective amount of one or more polymerization inhibitors or reducing agents to substantially stop any polymerization,” includes, but is not limited to, adding an amount of polymerization inhibitors or reducing agents generally from 25 to 5,000 ppm, preferably from 50 to 3,500 ppm based on polymer solids, or in amounts exceeding these ranges, and/or wherein no appreciable free-radical content remains in the reactor including the multistage polymer and unreacted monomer.

#### *B. Obviousness over Touda*

Petitioner contends that claims 1–6 would have been obvious over Touda (Ex. 1003) under 35 U.S.C. § 103(a). Pet. 5, 20–29. Touda discloses:

A process for producing polymer particles containing one microvoid or two or more discrete microvoids, which comprises (1) adding a base to a latex of a carboxyl-modified copolymer containing 0.1 to 1000 parts of an organic solvent per 100 parts by weight of the carboxyl-modified copolymer to neutralize at least part of the carboxyl groups in the copolymer, and (2) adding an acid to the latex to adjust the pH of the latex to not more than 7.

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Ex. 1003, Abstract.

Touda explains that:

[T]he present inventors have found that if the polymer particles are swollen with a base in the presence of an organic solvent, microvoid-containing polymer particles can be obtained easily with a short period of time, and microvoid-containing particles of a polymer having a high glass transition temperature can be obtained, and that this process can also give polymer particles having a plurality of microvoids.

*Id.* at 2:41–48.

Further, Touda teaches that “[t]here is no particular limitation on the method of obtaining polymers containing carboxyl groups,” and discloses that the method may include copolymerizing carboxyl-containing monomers, which “is advantageous to production.” *Id.* at 2:66–3:4. Touda discloses that exemplary carboxyl-containing monomers that can be used in the invention include ethylenically unsaturated carboxylic acids, such as methacrylic acid, and that exemplary monomers, which are copolymerizable with carboxyl-containing monomers, include aromatic vinyl monomers, such as styrene. *Id.* at 3:5–8, 25–29.

Additionally, Touda teaches that “[t]here is no particular restriction on the method of including an organic solvent in the carboxyl-modified copolymer latex,” and the method may, for example, involve adding an organic solvent to a latex obtained by polymerization. *Id.* at 3:61–64. The organic solvent used in the invention also is not particularly limited, as long as it “can fully swell the copolymer particles.” *Id.* at 3:66–4:1. Touda discloses specific examples of solvents, including toluene. *Id.* at 4:1–3.

Petitioner asserts that Touda discloses each and every element of claim 1 of the ’004 patent. Pet. 20. According to Petitioner, “*Touda*

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expressly discloses all but two of the elements of claim 1 of the '004 patent in a single example – Example 2 (combination of Examples 1S, 2A and 2B).” *Id.* at 20 (citing Ex. 1002 ¶ 55). Petitioner asserts that the two elements not disclosed in Touda Example 2 are taught expressly elsewhere in the disclosure of Touda. *Id.*

Touda discloses in Example 1S the “[s]ynthesis of a seed latex,” comprising: placing 300 parts of deionized water in a reactor, along with 95 parts of styrene (i.e., 95% of a nonionic monoethylenically unsaturated monomer), and 5 parts of MAA (i.e., 5% of a hydrophilic monoethylenically unsaturated monomer); heating and stirring the mixture; allowing the temperature of the mixture to reach 70° C and then adding 17 parts of a 3% aqueous solution of potassium persulfate; and maintaining the reaction mixture at 70° C for three hours to complete the polymerization reaction, resulting in a polymerization conversion of 99%. Ex. 1004, 6:33–49; Pet. 36.

Touda discloses in Example 2A the “[p]roduction of a filled polymer latex in the presence of an organic solvent,” comprising charging the same reactor used in the production of the seed latex with 508 parts of deionized water, 3.4 parts of seed latex [S]; heating the contents to 80° C; adding 30 parts of a 3% aqueous solution of potassium persulfate; adding a mixture of a monomeric mixture composed of 87.7 parts of styrene (i.e., at least 50% by weight of nonionic monoethylenically unsaturated monomer), 0.3 parts of divinylbenzene, 5 parts of methyl methacrylate and 7 parts of MAA and *10 parts of toluene* over 6 hours; and then maintaining the mixture at 80° C for 2 hours to complete the polymerization reaction. Ex. 1004, 7:35–56.

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Touda discloses in Example 2B the production of a microvoid-containing latex, comprising: charging the same reactor used in the production of the seed latex with 870 parts of deionized water, 100 parts of the filled polymer latex, 1 part of sodium dodecyl-benzenesulfate, 50 parts of *toluene*, and 33 parts of a 10% aqueous solution of sodium hydroxide; stirring the mixture at 80° C for three hours; adding 300 parts of a 1% aqueous solution of hydrochloric acid; stirring the mixture at 80° C for 3 hours; cooling the reaction mixture to room temperature; and removing the organic solvent under reduced pressure. *Id.* at 7:58–62; *see also id.* at 7:4–24.

Petitioner asserts that although Touda Example 2 does not expressly disclose adding an effective amount of one or more polymerization inhibitors to substantially stop any polymerization, it would have been obvious to a person of ordinary skill in the art at the time the invention was made to have modified the process of Touda's Example 2A by substituting 10 parts of cresol, an organic solvent and polymerization inhibitor, in place of the disclosed 10 parts of toluene organic solvent. Pet. 23. Petitioner reasons that the artisan would have been motivated to make this modification because Touda teaches that there is no particular restriction on the type of organic solvent used, and explicitly discloses cresol as an exemplary organic solvent. *Id.* at 22 (citing Ex. 1003, 3:61–63,4:7).

Patent Owner asserts a person of ordinary skill in the art would have understood that cresol is an inhibitor, and that substituting it for toluene in Touda's Example 2A would have “shut down the polymerization reaction.” PO Resp. 41 (citing Ex. 2005 ¶ 128). Patent Owner asserts that in Example 2A, toluene is added as part of a mixture including monomers during a “6-

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hour polymerization step that results in the formation of the shell polymer as part of a ‘filled polymer latex.’” *Id.* at 41 (citing Ex. 1003, 7:34–55).

Therefore, Patent Owner asserts that a person of ordinary skill in the art would not use cresol, a polymerization inhibitor, in place of toluene, during this step because doing so would prevent polymerization and formation of the shell polymer. *Id.* (citing Ex. 2005 ¶ 128).

Petitioner acknowledges that substituting cresol for toluene “shortstops the polymerization reaction.” Pet. Reply 2–3. However, Petitioner asserts that doing so does not prevent the formation of a multistage polymer particle. *Id.* In support of this assertion, Petitioner relies on experimental results detailed in the Declaration of Dr. Schork, Patent Owner’s witness. According to Petitioner, Dr. Schork’s experiment involving substituting cresol for toluene in Touda’s Example 2A, “confirms that a meaningful amount of shell stage polymer (approximately 17 wt. % based on wt. % of the multi-stage polymer particle) was formed.” *Id.* at 3 (citing Ex. 2005 ¶ 128, Ex. I), 13 (citing Ex. 1001, 7:24–27).

After considering the arguments and evidence, we find that Patent Owner has established that a person of ordinary skill in the art would not have been motivated to substitute cresol for toluene in step 2A of Touda’s Example 2. Although cresol and toluene are both solvents, Patent Owner has established with persuasive evidence that cresol’s additional function as a polymerization inhibitor would have defeated the purpose of the solvent in Touda’s step 2A. That step is directed to the production of a filled polymer latex (multi-stage polymer). Ex. 1003, 7:35–56. During step 2A, toluene was added to a monomeric mixture over the course of 6 hours. *Id.* at 7:49–50. Then the mixture was maintained at 80 °C for 2 hours to complete the

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polymerization reaction. *Id.* at 7:51–52.

Dr. Schork attempted to replicate Example 2 with cresol substituting for toluene during step 2A, as proposed by Petitioner. Ex. 2005 ¶¶ 92–95 (citing Declaration Ex. I, “Synthesis Procedure for Touda ’320 Example 2 Modified”). Dr. Schork explained that the result observed from using cresol during step 2A was not surprising: “monomer was only 2.5% converted to polymer after the required eight hours.” *Id.* ¶ 95. Dr. Schork stated, “[i]n my opinion, these results show that the modified process of Example 2A does not make a core-shell emulsion polymer having a core stage and a shell stage because the cresol inhibits polymerization during the phase intended to make the shell.” *Id.* Petitioner’s assertion to the contrary—that Dr. Schork’s experiment produced “a meaningful amount of shell stage polymer,”—is merely attorney argument unsupported by any persuasive evidence. Pet. Reply 13. Indeed, Petitioner’s Declarant, Marek W. Urban, Ph.D., did not attempt to replicate Example 2 with the modifications proposed by Petitioner, i.e., substituting cresol for toluene in Step 2A.

Accordingly, we conclude that Petitioner has not established that it would have been obvious to modify Touda’s Example 2 to include a polymerization inhibitor.

Moreover, we agree with Patent Owner that Touda’s Example 2 also does not include a swelling agent, as required by claim 1 of the ’004 patent. PO Resp. 28. In particular, as Patent Owner asserts, Touda does not disclose expressly sodium hydroxide, or any other base, as a “swelling agent,” i.e., being capable of permeating the shell and swelling the core of the emulsion polymer under the conditions of Example 2. *Id.*

Petitioner asserts that even if our construction of “swelling agent”

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requires a base that permeates the shell and swells the core, Petitioner “has established a *prima facie* case of inherency under Office practice.” Pet. Reply 10 (citing *In re Best*, 562 F.2d 1252, 1254 (C.C.P.A. 1977); *In re Spada*, 911 F.2d 705, 707–08 n.3 (Fed. Cir. 1990); *In re Mousa*, 479 F. App’x. 348, 353 (Fed. Cir. 2012)), 14. According to Petitioner, sodium hydroxide inherently permeates the shell and swells the core of the polymer particles in Touda because the same polymer particles are described in the ’004 patent as suitable for swelling. Pet. Reply 14.

However, Dr. Schork explains that in Touda’s Example 1S, the core is only 5 parts (5%) methacrylic acid and the shell in Example 2A is only 6 parts (6%) acrylic acid, such that the core and the shell are only slightly acidic. Ex. 2005 ¶ 77. Dr. Schork states that a person of skill in the art “would understand that under these conditions, NaOH would at best neutralize the shell, not the core.” *Id.* According to Dr. Schork, “[g]iven the low levels of acid, the NaOH would be unlikely to permeate and neutralize any part of the particle. Certainly, NaOH would not permeate the shell and swell the core. Instead, to the extent that any swelling occurred, it would take place in the shell.” *Id.* Again, we are persuaded by Dr. Schork’s testimony and do not find that Petitioner has provided persuasive evidence contradicting Dr. Schork’s opinion.

Accordingly, after considering the arguments and evidence, and based upon our construction of the term “swelling agent,” we find that Petitioner has not established that Touda discloses sodium hydroxide as a “swelling agent” in the process of Example 2.

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Based on the foregoing discussion and the record, we conclude that Petitioner has not shown by a preponderance of the evidence that claims 1–6 would have been obvious over Touda under 35 U.S.C. § 103(a).

*C. Obviousness over Touda and Overbeek*

Petitioner contends that claim 7 would have been obvious over Touda and Overbeek under 35 U.S.C. § 103(a). Pet. 6, 29–30. Claim 7 recites, “The process of claim 1 wherein the level of monomer is reduced to less than 10,000 ppm based on polymer solids by polymerizing said monomer.” Petitioner asserts that Touda teaches or suggests each element of independent claim 1, and combines Overbeek with Touda to teach the further limitation of dependent claim 7, i.e., that the level of monomer in the emulsion is “reduced to less than 10,000 ppm based on polymer solids by polymerizing said monomer.” Pet. 18, 29.

Because Petitioner relies on Touda as teaching or suggesting adding a “swelling agent” and one or more “polymerization inhibitors,” in the same manner set forth regarding claim 1, we conclude that Petitioner has not shown by a preponderance of the evidence that claim 7 would have been obvious over Touda and Overbeek under 35 U.S.C. § 103(a).

*D. Obviousness over Toda and Crouch*

Petitioner asserts that claims 1–7 would have been obvious over Toda (Ex. 1004) and Crouch (Ex. 1006) under 35 U.S.C. § 103(a). Pet. 6, 38–46.

Toda discloses:

A process for preparation of latex of a hollow polymer which comprises adding a base, in the presence of a monomer, to latex containing carboxy-modified copolymer particles to make the pH of the latex 8 or more; adding a carboxyl group-containing monomer to make the pH of the latex 7 or less; and then polymerizing these monomers.



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Ex. 1004, Abstract.

In Example 11, Toda discloses a process for obtaining a latex containing polymer particles comprising the steps of forming a center layer, an intermediate layer, and a surface layer. *Id.* at 11:59–68; 12:13–37; 12:61–68; 13:1–2; Table 2. The center layer was formed by placing in a reactor 400 parts of deionized water, 0.3 part of monomer mixture (a) (i.e., 70% of methyl methacrylate (“MMA”), 5% of butyl acrylate (“BA”) and 25% of MAA, and 0.3 part of an emulsifier; heating the mixture to 80° C and stirring to prepare an emulsion; adding 7 parts of aqueous 3% potassium sulfate (“KPS”) solution; subjecting the mixture to polymerization at 80° C for 0.5 hour to obtain seed particles; adding 0.5 part of an emulsifier; continuously adding the residual monomer mixture (a) over a period of one hour; and carrying out polymerization for 2 hours, resulting in a conversion of monomer mixture (a) of 98%. *Id.* An intermediate layer was formed by adding to the reactor 7 parts of KPS; continuously adding monomer mixture (b) (i.e., 87% of MMA, 10% of BA and 3% of MAA); and carrying out polymerization for 4 hours, resulting in a conversion of mixture (b) of 98%. The surface layer was formed by adding 7 parts of KPS to the reactor; continuously adding a monomer (c), i.e., 100% of styrene; and carrying out polymerization for 4 hours, lowering the temperature to 20° C to obtain latex-containing polymer particles, wherein the conversion of monomer mixture (c) was 98%. *Id.*

Toda further discloses in Example 11: (i) adding 3 parts of styrene to the obtained latex containing polymer particles to soften the particles; adding aqueous 10% potassium hydroxide solution and heating to 80° C for 3 hours (base treatment); (ii) adding 80 parts of aqueous MAA and 50 parts

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of styrene and stirring the mixture at 80° C for 3 hours (acid treatment); and (iii) adding 10 parts of aqueous 3% KPS solution, stirring the mixture of unreacted monomers at 80°C for 2 hours to carry out copolymerization, resulting in a polymerization conversion at this final stage of 99%. *Id.* at 12:38–59, Table 2.

Petitioner asserts that Toda discloses, in at least Example 11, each and every element of claims 1–7 of the '004 patent, except for adding a polymerization inhibitor. Pet. 39–41. Petitioner asserts that Toda, “however, teaches that ‘[w]hen it is desired to make a base treatment at a lower temperature, it is sufficient to lower polymerization conversion’ and suggests polymerization conversions of 83% to 99%.” *Id.* at 41 (citing Ex. 1004, 6:43–48). Toda does not specifically explain how to lower the polymerization conversion, but Petitioner asserts that Crouch discloses “adding hydroquinone [a polymerization inhibitor] or other novel reducing agents to a polymerizing emulsion to substantially stop polymerization after a desired degree of polymerization has been obtained.” *Id.* (citing Ex. 1002 ¶¶ 88–89). Petitioner contends, therefore, that in view of the combined teachings of Toda and Crouch, it would have been obvious to one of ordinary skill in the art to add hydroquinone in the process of Toda’s Example 11 to shortstop the emulsion polymerization, lower the monomer conversion, and to lower the temperature during which the base treatment is conducted by adding hydroquinone, as taught by Crouch. *Id.* at 42.

Based on our construction of the term “swelling agent,” and in consideration of the arguments and evidence, we find that the Petitioner has not established persuasively that the process disclosed in Toda’s Example 11 includes adding a “swelling agent.” According to Petitioner, in Example 11,

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“[i]mmediately after the ‘softening step,’ aqueous potassium hydroxide solution was added as a swelling agent.” Pet. 43. Petitioner supports this position by referring to Toda’s disclosure of adding potassium hydroxide solution in the process of Example 11, Pet. 43 (citing Ex. 1004, 12:40–43, Table 2) and the testimony of Petitioner’s Declarant, Dr. Urban, who explains that potassium hydroxide “is a fixed base expressly identified by the ’004 patent as a possible swelling agent” (Ex. 1002 ¶ 92)).

In the Response, Patent Owner asserts that Toda does not describe potassium hydroxide as being “capable of permeating the shell and swelling the core” of the multi-stage emulsion polymer prepared by Example 11. PO Resp. 33. Further, Patent Owner asserts that a person of ordinary skill in the art would not understand the potassium hydroxide disclosed in Toda to be a “swelling agent.” *Id.* (citing Ex. 2005 ¶ 99). In Toda’s Example 11, the reaction temperature is lowered to 20 °C before adding the potassium hydroxide. *Id.* (citing Ex. 1004, 12:34–36). According to Dr. Schork, a person of ordinary skill in the art would understand that at that temperature, the polystyrene shell would be too hard for potassium hydroxide to permeate it. Ex. 2005 ¶¶ 100, 149. Additionally, Dr. Schork explained that a person of ordinary skill would understand that after the reaction is heated back up to 80 °C, the shell would still be too rigid for potassium hydroxide “to permeate under the conditions of the base treatment with ‘3 parts of styrene.’” *Id.* ¶149.

Further, Patent Owner asserts that Dr. Schork’s attempt to replicate the process of Example 11 confirms that the added potassium hydroxide is not a “swelling agent.” *Id.* at 33, 56 (citing Ex. 2005 ¶¶ 117–120). According to Dr. Schork, his replication of Example 11, incorporating the

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modification proposed by Petitioner (i.e., adding hydroquinone to shortstop the reaction monomer mixture (c)), provided “no evidence of swelling during the base treatment step.” Ex. 2005 ¶147.

In its Reply, Petitioner argues that even if our construction of “swelling agent” requires a base that permeates the shell and swells the core, Toda discloses such a system. Pet. Reply 14. According to Petitioner, potassium hydroxide inherently permeates the shell and swells the core of the polymer particles in Toda because the same polymer particles are described in the ’004 patent as suitable for swelling. *Id.*

As discussed previously, we have construed the claim term “swelling agent” as encompassing a structure, i.e., a base, and a function, i.e., being capable of permeating the shell and swelling the core, in the presence of the multistage polymer and monomer, under the conditions of the specific process for which the agent is to be used. We are not persuaded by Petitioner’s assertion that potassium hydroxide permeates the shell and swells the core of the polymer particles in Toda merely because the same polymer particles are described in the ’004 patent as suitable for swelling. Pet. Reply 14. In Toda’s Example 11, the potassium hydroxide was added to the mixture after the temperature of the mixture was lowered to 20° C and styrene was added to soften the polymer particles. Ex. 1004, 12:38–42. Patent Owner provides persuasive evidence, through the Declaration of Dr. Schork, that a person of ordinary skill in the art would have understood that the shell would be too hard at this temperature for potassium hydroxide to be capable of permeating the shell and swelling the core. PO Resp. 33–34 (citing Ex. 2005 ¶ 100). Petitioner has not argued persuasively otherwise. *See, e.g.*, Pet. Reply 13–14.

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Further, in Toda's Example 11, after adding the potassium hydroxide, the mixture is heated to 80 °C. Ex. 1003, 12:41–44. Patent Owner provides persuasive evidence, also through the Declaration of Dr. Schork, that based on the teachings of Toda, a person of ordinary skill in the art would not expect potassium hydroxide to permeate the shell and swell the core at that temperature either. PO Resp. 34 (citing Ex. 2005 ¶ 100). Petitioner has not argued persuasively otherwise. *See, e.g.*, Pet. Reply 13–14.

Additionally, Patent Owner provides persuasive experimental evidence that the potassium hydroxide solution used in Toda's Example 11 is not capable of permeating the shell and swelling the core. *See* PO Resp. 33, 36, 56 (citing Ex. 2005 ¶¶ 117–120). Dr. Schork replicated Toda's Example 11, incorporating the modification proposed by Petitioner, i.e., adding hydroquinone to shortstop the reaction monomer mixture (c). Ex. 2005 ¶¶ 117–118. Dr. Schork explained that after the potassium hydroxide was added, “the heating of the reactor back to 80 °C was initiated, but was not achieved because the entire reactor gelled to a viscous mass that could not be stirred.” *Id.* ¶ 119. Dr. Schork stated, “TEM [transition electron microscopy] data of the final product and in-process samples ([Declaration] Ex. P) confirms that modified Example 11 did not result in voided or swollen emulsion particles.” *Id.* ¶ 120. Indeed, according to Dr. Schork, modified Example 11 did not even produce multi-stage emulsion particles with a separate core and shell. *Id.* Dr. Schork concluded, “Based on my replication of Example 11, including analysis of the TEM images, there is no evidence of swelling during the base treatment step.” Ex. 2005 ¶147.

Petitioner has not provided any experimental data or evidence contradicting Dr. Schork's results and findings.

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Accordingly, after considering the arguments and evidence, and based upon our construction of the term “swelling agent,” we find that Petitioner has not shown that Toda discloses potassium hydroxide as a “swelling agent” in the process of Example 11.

Based on the foregoing discussion and the record, we conclude that Petitioner has not shown by a preponderance of the evidence that Toda and Crouch render obvious claims 1–7.

### III. MOTION TO AMEND

Patent Owner’s Motion to Amend is contingent on claims of the ’004 patent being held unpatentable. Mot. Amend 1. Because these claims are not held to be unpatentable, there is no occasion to reach or decide the motion to amend.

### IV. CONCLUSION

Petitioner has not demonstrated by a preponderance of the evidence that claims 1–7 instituted for *inter partes* review are unpatentable under 35 U.S.C. § 103(a) as obvious over Touda, Touda and Overbeek, or Toda and Crouch.

### ORDER

In consideration of the foregoing, it is hereby:

ORDERED that Petitioner’s request for cancellation of claims 1–7 of the ’004 patent is *denied*;

FURTHER ORDERED that Patent Owner’s Motion to Amend is *dismissed* as moot; and

FURTHER ORDERED that, because this is a Final Written Decision, parties to the proceeding seeking judicial review of the decision must comply with the notice and service requirements of 37 C.F.R. § 90.2.

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United States Patent

Blankenship et al.

[19]

Patent Number:

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6,020,435

Feb. 1, 2000

[54] PROCESS FOR PREPARING POLYMER CORE SHELL TYPE EMULSIONS AND POLYMERS FORMED THEREFROM

4,468,498 8/1984 Kowalski et al. .... 525/301

4,594,363 6/1986 Blankenship et al. .... 521/68

5,360,827 11/1994 Toda et al. .... 521/57

5,494,971 2/1996 Blankenship .... 525/301

5,521,253 5/1996 Lee et al. .... 525/301

5,639,805 6/1997 Park .... 523/201

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[21] Appl. No.: 08/974,763

[22] Filed: Nov. 20, 1997

Related U.S. Application Data

[60] Provisional application No. 60/064,513, Nov. 5, 1997.

[51] Int. Cl.<sup>7</sup> ..... C08F 4/00

[52] U.S. Cl. .... 525/256; 525/263; 525/301; 525/902

[58] Field of Search ..... 525/309, 244, 525/301, 264, 263, 256, 261

[56] References Cited

U.S. PATENT DOCUMENTS

4,427,836 1/1984 Kowalski et al. .... 525/301

FOREIGN PATENT DOCUMENTS

WO 95/11265 4/1995 WIPO .

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[57] ABSTRACT

A process for preparing multi-stage emulsion polymers is provided. The process is capable of producing multi-stage emulsion polymers having low dry-bulk density. These polymers are useful in coating compositions such as paints and paper coatings.

5 Claims, No Drawings



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# PROCESS FOR PREPARING POLYMER CORE SHELL TYPE EMULSIONS AND POLYMERS FORMED THEREFROM

This application claims benefit of Provisional Application 60,064,513 filed Nov. 5, 1997.

The present invention relates to processes for preparing polymer emulsions and polymers formed therefrom. In particular, the present invention relates to aqueous emulsion polymerization processes for preparing polymer emulsions and emulsion polymers formed therefrom.

"Emulsion polymer", as used herein, refers to a water-insoluble polymer which is prepared by emulsion polymerization techniques.

"Polymer emulsion", as used herein, refers to an aqueous composition having discrete, water-insoluble polymer particles dispersed therein.

As used herein, acrylate and methacrylate are referred to as "(meth)acrylate," acrylic acid and methacrylic acid are referred to as "(meth)acrylic acid."

Emulsion polymers, such as hollow or voided emulsion polymers, are known for use in several industrial applications. The literature uses the terms "hollow" and "voided" interchangeably. These polymers are often used in paints, coatings, inks, sunscreens and paper manufacture. Hollow emulsion polymers are generally prepared by swelling a core/shell emulsion polymer in such a way that one or more voids form in the interior of the emulsion polymer particle. These voids contribute, among other things, to the opacity of coatings and films prepared with the hollow emulsion polymer.

For some applications, it is particularly desirable to minimize the weight of the coating applied. For example, it is desirable for certain paper coatings applications to have a high performance coating without adding considerably to the weight of the paper.

Accordingly, it is desirable to provide lightweight, low density additives for coatings, such as voided latex particles.

Voided latex particles can be prepared by any of several known process, including those described U.S. Pat. Nos. 4,427,836, 4,468,498, 4,594,363, 4,880,842, 5,494,971, 5,521,253, 5,157,084, 5,360,827 among others. Voided latex particles, as described in the references noted above, are prepared by swelling the core of a core-shell emulsion polymer. Some of the processes, such as that described by U.S. Pat. No. 5,360,827 describe the processes whereby, in the latter stages of polymerizing the shell, monomer is added to facilitate diffusion of base into the core of the polymer in order to achieve swelling. Then, the pH of the emulsion is adjusted with a carboxyl-group containing monomer which is subsequently polymerized. However, this process is time consuming and does not result in suitable lightweight emulsion polymers.

The present invention seeks to overcome the deficiencies in the previously known processes by providing low density voided emulsion polymers and a process for preparing them.

In a first aspect of the present invention, there is provided a process for preparing emulsion polymer particles comprising:

- a) providing an aqueous emulsion of
- i) multi-stage emulsion polymer, comprising a core stage polymer and a shell stage polymer, wherein the core stage polymer comprises, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core stage polymer, of hydrophilic monoethylenically unsaturated monomer, and from 0 to 95 percent by weight, based on the weight of the

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core stage polymer, of at least one nonionic monoethylenically unsaturated monomer; and wherein the shell stage polymer comprises, as polymerized units, at least 50 percent by weight of nonionic monoethylenically unsaturated monomer;

ii) monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer; and

iii) swelling agent

under conditions wherein there is no substantial polymerization of the monomer; and

b) reducing the level of monomer by at least fifty percent.

In a second aspect of the present invention, there is provided an aqueous polymer emulsion comprising water and swollen multi-stage emulsion polymer wherein the dry bulk density of the swollen multi-stage emulsion is: less than 0.77 grams per cubic centimeter ("g/cc") when the swollen multi-stage emulsion polymer has a particle size below 275 nanometers ("nm"); less than 0.74 g/cc when the swollen multi-stage emulsion polymer has a particle size of from 275 to 500 nm; less than 0.59 g/cc when the swollen multi-stage emulsion polymer has a particle size of from 501 to 750 nm; less than 0.46 g/cc when the swollen multi-stage emulsion polymer has a particle size of from 751 to 1300 nm.

The stages of the multi-stage polymers of the present invention include core stage polymer (the "core"), and shell stage polymer (the "shell"). The core and shell may themselves be comprised of more than one stage. There may also be one or more intermediate stages. Preferably, the multi-stage polymer comprises a core, an intermediate layer and a shell.

The cores of the multi-stage polymers of the present invention are emulsion polymers comprising, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core, of at least one hydrophilic monoethylenically unsaturated monomer and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer.

Cores containing at least five percent by weight, based on the total weight of the core polymer, of at least one hydrophilic monoethylenically unsaturated monomer will generally result in a suitable degree of swelling. There may be instances wherein, because of the hydrophobicity of certain comonomers or combinations thereof in conjunction with the hydrophobic/hydrophilic balance of a particular hydrophilic monomer, the copolymer may be suitably prepared with less than five percent by weight, based on the total weight of the core polymer, of a hydrophilic monoethylenically unsaturated monomer. Preferably, the core comprises, as polymerized units, hydrophilic monoethylenically unsaturated monomer at a level of from 5 to 100, more preferably, from 20 to 60, and most preferably, from 30 to 50 percent by weight based on the total weight of the core. The hydrophilic core polymer may be made in a single stage or step of the sequential polymerization or may be made by a plurality of steps in sequence.

The multi-stage emulsion polymer of the present invention contemplates a core polymer wherein at least one hydrophilic monoethylenically unsaturated monomer is polymerized alone or with at least one nonionic monoethylenically unsaturated monomer. This process also contemplates, and includes in the term "hydrophilic monoethylenically unsaturated monomer," the use of a nonpolymeric compound containing at least one carboxylic acid group which absorbed into the core polymer before, during or after the polymerization of the hydrophobic shell polymer as a replacement for the hydrophilic monoethylenically

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unsaturated monomer in the hydrophilic core polymer, as described in U.S. Pat. No. 4,880,842. In addition, this invention contemplates, and includes in the term "hydrophilic monoethylenically unsaturated monomer," the use of a latent hydrophilic core polymer which contains no hydrophilic monoethylenically unsaturated monomer but which is swellable upon hydrolysis to a hydrophilic core polymer as described in U.S. Pat. No. 5,157,084.

Suitable hydrophilic monoethylenically unsaturated monomer useful for making the core polymer include monoethylenically unsaturated monomers containing acid-functionality such as monomers containing at least one carboxylic acid group including acrylic acid, methacrylic acid, acryloxypropionic acid, (meth)acryloxypropionic acid, itaconic acid, aconitic acid, maleic acid or anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, monomethyl itaconate and the like. Acrylic acid and methacrylic acid are preferred.

Suitable nonpolymeric compounds containing at least one carboxylic acid group include  $C_6$ - $C_{12}$  aliphatic or aromatic monocarboxylic acids and dicarboxylic acids, such as benzoic acid, m-toluic acid, p-chlorobenzoic acid, o-acetoxybenzoic acid, azelaic acid, sebacic acid, octanoic acid, cyclohexanecarboxylic acid, lauric acid and monobutyl phthalate and the like.

Suitable nonionic monoethylenically unsaturated monomers for making the hydrophilic core polymer include styrene, a-methyl styrene, p-methyl styrene, t-butyl styrene, vinyltoluene, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, (meth)acrylonitrile, (meth)acrylamide,  $(C_1-C_{20})$  alkyl or  $(C_3-C_{20})$  alkenyl esters of (meth)acrylic acid, such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate and the like.

The core, whether obtained by a single stage process or a process involving several stages, has an average particle size of from 50 nm to 1.0 micron, preferably from 100 nm to 300 nm, diameter in unswollen condition. If the core is obtained from a seed polymer, the seed polymer preferably has an average particle size of from 30 nm to 200 nm.

The core may also optionally contain less than 20 percent by weight, preferably from 0.1 to 3 percent by weight, based on the total weight of the core, of polyethylenically unsaturated monomer, wherein the amount used is generally approximately directly proportional to the amount of hydrophilic monoethylenically unsaturated monomer used; in other words, as the relative amount of hydrophilic monomer increases, it is acceptable to increase the level of polyethylenically unsaturated monomer. Alternatively, the core polymer may contain from 0.1 to 60 percent by weight, based on the total weight of the core polymer, of butadiene.

Suitable polyethylenically unsaturated monomers include comonomers containing at least two addition polymerizable vinylidene groups and are alpha beta ethylenically unsaturated monocarboxylic acid esters of polyhydric alcohols containing 2-6 ester groups. Such comonomers include alkylene glycol diacrylates and dimethacrylates, such as for example, ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate propylene glycol diacrylate and triethylene glycol dimethylacrylate; 1,3-glycerol dimethacrylate; 1,1,1-trimethylol propane dimethacrylate; 1,1,1-trimethylol ethane diacrylate; pentaerythritol trimethacrylate; 1,2,6-hexane triacrylate; sorbitol pentamethacrylate; methylene

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bis-acrylamide, methylene bis-methacrylamide, divinyl benzene, vinyl methacrylate, vinyl crotonate, vinyl acrylate, vinyl acetylene, trivinyl benzene, triallyl cyanurate, divinyl acetylene, divinyl ethane, divinyl sulfide, divinyl ether, divinyl sulfone, diallyl cyanamide, ethylene glycol divinyl ether, diallyl phthalate, divinyl dimethyl silane, glycerol trivinyl ether, divinyl adipate; dicyclopentenyl (meth)acrylates; dicyclopentenyl (meth)acrylates; unsaturated esters of glycol monodicyclopentenyl ethers; allyl esters of  $\alpha,\beta$ -unsaturated mono- and dicarboxylic acids having terminal ethylenic unsaturation including allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl itaconate and the like.

The multi-stage polymer of the present invention preferably contains an intermediate stage. The intermediate stage polymer, when present, partially or fully encapsulates the core and itself is partially or fully encapsulated by the shell. The intermediate stage is prepared by conducting an emulsion polymerization in the presence of the core.

The intermediate stage preferably contains, as polymerized units, from 0.3 to 20, more preferably from 0.5 to 10 percent by weight, based on the weight of the core, of at least one hydrophilic monoethylenically unsaturated monomer. The intermediate stage preferably contains, as polymerized units, from 80 to 99.7, more preferably from 90 to 99.5 percent by weight, based on the weight of the intermediate stage, of at least one nonionic monoethylenically unsaturated monomer. The hydrophilic monoethylenically unsaturated monomers and the nonionic monoethylenically unsaturated monomers useful for making the core are also useful for making the intermediate layer.

The shell of the multi-staged polymer of this invention is the product of emulsion polymerizing from 80 to 100, preferably from 90 to 100, percent by weight, based on the total weight of the shell, of at least one nonionic monoethylenically unsaturated monomer. The nonionic monoethylenically unsaturated monomers suitable for the core are also suitable for the shell. Styrene is preferred.

The shell may also contain, as polymerized units, from 0 to 20, preferably from 0 to 10, percent by weight based on the weight of the shell, of one or more monoethylenically unsaturated monomers containing acid-functionality for making the hydrophobic polymer shell include acrylic acid, methacrylic acid, acryloxypropionic acid, (meth)acryloxypropionic acid, itaconic acid, aconitic acid, maleic acid, maleic anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, monomethyl itaconate and the like. Acrylic acid and methacrylic acid are preferred.

The monomers used and the relative proportions thereof in the shell should be such that it is permeable to an aqueous or gaseous volatile or fixed basic swelling agent capable of swelling the core. Monomeric mixtures for making the shell preferably contain from about 0.1% by weight to about 10% by weight, based on the total weight of the shell polymer, of an acid-functional monoethylenically unsaturated monomer. Preferably, the proportion of acid-functional monoethylenically unsaturated monomer in the shell polymer does not exceed one-third the proportion thereof in the core polymer.

The presence of acid-functional monoethylenically unsaturated monomer in the shell polymer may serve several functions:

(1) stabilizing of the final multi-stage emulsion polymer; and  
(2) assuring permeability of the shell to a swelling agent;

(3) compatibilizing the shell with the previously formed stage of the multistage emulsion polymer.

As used herein, the term "sequentially emulsion polymerized" or "sequentially emulsion produced" refers to poly-

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mers (including homopolymers and copolymers) which are prepared in aqueous medium by an emulsion polymerization process in the presence of the dispersed polymer particles of a previously formed emulsion polymer such that the previously formed emulsion polymers are increased in size by deposition thereon of emulsion polymerized product of one or more successive monomer charges introduced into the medium containing the dispersed particles of the preformed emulsion polymer.

In the sequential emulsion polymerization with which the present invention is concerned, the term "seed" polymer is used to refer to an aqueous emulsion polymer dispersion which may be the initially-formed dispersion, that is, the product of a single stage of emulsion polymerization or it may be the emulsion polymer dispersion obtained at the end of any subsequent stage except the final stage of the sequential polymerization. Thus, a hydrophilic core polymer which is herein intended to be encapsulated by one or more subsequent stages of emulsion polymerization may itself be termed a seed polymer for the next stage.

The method of this invention contemplates that the core, the intermediate stage, the shell, or any combination thereof may be made in a single stage or step of the sequential polymerization or may be made by a plurality of steps in sequence following the polymerization. The first stage of emulsion polymerization in the process of the present invention may be the preparation of a seed polymer containing small dispersed polymer particles insoluble in the aqueous emulsion polymerization medium. This seed polymer may or may not contain any hydrophilic monomer component but provides particles of minute size which form the nuclei on which the hydrophilic core polymer, with or without non-ionic comonomer, is formed.

A water-soluble free radical initiator is utilized in the aqueous emulsion polymerization. Suitable water-soluble free radical initiators include hydrogen peroxide; tert-butyl peroxide; alkali metal persulfates such as sodium, potassium and lithium persulfate; ammonium persulfate; and mixtures of such initiators with a reducing agent. Reducing agents include: sulfites, such as alkali metal metabisulfite, hydrosulfite, and hyposulfite; sodium formaldehyde sulfoxylate; and reducing sugars such as ascorbic acid and isoascorbic acid. The amount of initiator is preferably from 0.01 to 3 percent by weight, based on the total amount of monomer and in a redox system the amount of reducing agent is preferably from 0.01 to 3 percent by weight based on the total amount of monomer. The temperature may be in the range of about 10° C. to 100° C. In the case of the persulfate systems, the temperature is preferably in the range of 60° C. to 90° C. In the redox system, the temperature is preferably in the range of 30° C. to 70° C., preferably below about 60° C., more preferably in the range of 30° C. to 45° C. The type and amount of initiator may be the same or different in the various stages of the multi-stage polymerization.

One or more nonionic or anionic emulsifiers, or surfactants, may be used, either alone or together. Examples of suitable nonionic emulsifiers include tert-octylphenoxyethylpoly(39)-ethoxyethanol, dodecyloxypoly(10)ethoxyethanol, nonylphenoxyethyl-poly(40)ethoxyethanol, polyethylene glycol 2000 monooleate, ethoxylated castor oil, fluorinated alkyl esters and alkoxylates, polyoxyethylene (20) sorbitan monolaurate, sucrose monococoate, di(2-butyl)phenoxypoly(20)ethoxyethanol, hydroxyethylcellulosepolybutyl acrylate graft copolymer, dimethyl silicone polyalkylene oxide graft copolymer, poly(ethylene oxide)poly(butyl acrylate) block

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copolymer, block copolymers of propylene oxide and ethylene oxide, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylated with 30 moles of ethylene oxide, N-polyoxyethylene (20)lauramide, N-lauryl-N-polyoxyethylene(3)amine and poly(10)ethylene glycol dodecyl thioether. Examples of suitable anionic emulsifiers include sodium lauryl sulfate, sodium dodecylbenzenesulfonate, potassium stearate, sodium dioctyl sulfosuccinate, sodium dodecylphenyloxide disulfonate, nonylphenoxyethylpoly(1)ethoxyethyl sulfate ammonium salt, sodium styrene sulfonate, sodium dodecyl allyl sulfosuccinate, linseed oil fatty acid, sodium or ammonium salts of phosphate esters of ethoxylated nonylphenol, sodium octoxynol-3-sulfonate, sodium cocoyl sarcosinate, sodium 1-alkoxy-2-hydroxypropyl sulfonate, sodium alpha-olefin (C<sub>14</sub>-C<sub>16</sub>)sulfonate, sulfates of hydroxyalkanols, tetrasodium N-(1,2-dicarboxy ethyl)-N-octadecylsulfosuccinamate, disodium N-octadecylsulfosuccinamate, disodium alkylamido polyethoxy sulfosuccinate, disodium ethoxylated nonylphenol half ester of sulfosuccinic acid and the sodium salt of tert-octylphenoxyethoxypoly(39)ethoxyethyl sulfate. The one or more surfactants are generally used at a level of from 0 to 3 percent based on the weight of the multi-stage polymer. The one or more surfactants can be added prior to the addition of any monomer charge, during the addition of a monomer charge or a combination thereof. In certain monomer/emulsifier systems for forming the shell, the tendency to produce gum or coagulum in the reaction medium may be reduced or prevented by the addition of about 0.05% to about 2.0% by weight, based on total weight of the shell polymer, of emulsifier without detriment to the deposition of the polymer formed on the previously formed core particles.

The amount of emulsifier may be zero, in the situation wherein a persulfate initiator is used, to 3 percent by weight, based on the weight of total weight of the core polymer. By carrying out the emulsion polymerization while maintaining low levels of emulsifier, the subsequent stages of polymerization deposit the most-recently formed polymer on the existing dispersed polymer particles resulting from the preceding step or stage. As a general rule, the amount of emulsifier should be kept below that corresponding to the critical micelle concentration for a particular monomer system, but while this limitation is preferable and produces a unimodal product, it has been found that in some systems the critical micelle concentration of the emulsifier may be exceeded somewhat without the formation of an objectionable or excessive number of dispersed micelles or particles. It is for the purpose of controlling the number of micelles during the various stages of polymerization so that the deposition of the subsequently formed polymer in each stage occurs upon the dispersed micelles or particles formed in the previous stages, that the concentration of emulsifier is kept low.

The viscosity- average molecular weight of the polymer formed in a given stage may range from 100,000, or lower if a chain transfer agent is used, to several million molecular weight. When 0.1% by weight to 20% by weight, based on the weight of the monomer, of a polyethylenically unsaturated monomer mentioned hereinbefore is used in making the core, the molecular weight is increased whether or not crosslinking occurs. The use of the polyethylenically unsaturated monomer reduces the tendency of the core polymer to dissolve when the multistaged polymer is treated with a swellant for the core. If it is desired to produce a core having a molecular weight in the lower part of the range, such as from 500,000 down to as low as about 20,000, it is frequently most practical to do so by avoiding the polyethyl-

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enically unsaturated monomers and using a chain transfer agent instead, such as 0.05% to 2% or more thereof, examples being alkyl mercaptans, such as sec-butyl mercaptan.

The weight ratio of core to the intermediate stage, if present, is generally in the range of from 1:0.5 to 1:10, preferably in the range of from 1:1 to 1:7. The weight ratio of core to shell is generally in the range of from 1:5 to 1:20, preferably in the range of from 1:8 to 1:15. When trying to decrease the dry density of the final product, is preferred to have as little shell as possible while still encapsulating the core.

The amount of polymer deposited to form shell polymer is generally such as to provide an overall size of the multistage polymer particle of from 70 nm to 4.5 microns, preferably from 100 nm to 3.5 microns, more preferably from 200 nm to 2.0 microns, in unswollen condition (that is, before any neutralization to raise the pH to about 6 or higher) whether the shell polymer is formed in a single stage or in a plurality of stages. In order to minimize the dry density of the final product, it is preferable to deposit only as much shell polymer as is needed to fully encapsulate the core. When the hydrophilic core polymer is fully encapsulated, it does not titrate with alkali metal bases under normal analytical conditions of about 1 hour and at room temperature. The extent of encapsulation can be determined by removing samples during the course of the shell polymerization and titrating with sodium hydroxide.

The multi-stage emulsion polymer is prepared by sequential emulsion polymerization, which, as discussed above, includes charging the monomers which form the shell. At, or near, the conclusion of charging the monomers which form the shell, the contents of the reactor include the multistage polymer, water and unreacted monomer. Under the conditions of an emulsion polymerization, there is also an appreciable free-radical content, or radical flux, which keeps the polymerization process going. Even if no additional monomer or initiator is added, there is an appreciable free-radical content in the system. When there is no appreciable free-radical content, in other words, when the radical flux is very low or approaches zero, then no substantial amount of polymerization will occur.

We have discovered that this free-radical content interferes with the extent of swelling which can be achieved. Previously known processes typically achieve swelling by adding a suitable swelling agent in the latter stages of charging the monomers which form the shell or at the completion of charging the monomers which form the shell. It is believed that the presence of unreacted monomer facilitates the transport of the swelling agent to the core. However, in previously known processes, the swelling agent was added to the system while there was still an appreciable free-radical content in the system. Thus, under those conditions, a substantial amount of polymerization was still occurring.

We have discovered that by providing an aqueous emulsion of the multi-stage emulsion polymer, monomer and swelling agent under conditions wherein there is no substantial polymerization of the monomer, we can enhance the extent of swelling of the multistage emulsion polymer.

There are many means for providing that no substantial polymerization of monomer is occurring, including the addition of one or more polymerization inhibitors, the addition of one or more reducing agents, waiting for a sufficient period of time until there are no longer an appreciable number of free-radicals by virtue of them terminating, cooling the contents of the reactor to limit the reactivity of

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the free-radicals, and combinations thereof. A preferred means involves the addition of one or more polymerization inhibitors such as, for example, N,N-diethylhydroxylamine, N-nitrosodiphenylamine, 2,4-dinitrophenylhydrazine, p-phenylenediamine, phenathiazine, alloocimene, triethyl phosphite, 4-nitrosophenol, 2-nitrophenol, p-aminophenol, 4-hydroxy-TEMPO (also known as 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy, free radical), hydroquinone, p-methoxyhydroquinone, tert-butyl-p-hydroquinone, 2,5-di-tert-butyl-p-hydroquinone, 1,4-naphthalenediol, 4-tert butyl catechol, copper sulfate, copper nitrate, cresol and phenol. When used, the polymerization inhibitors or reducing agents are added in effective amount to substantially stop any polymerization, generally from 25 to 5,000 parts per million ("ppm"), preferably from 50 to 3,500 ppm based on polymer solids. Preferably, the polymerization inhibitor(s) or reducing agent(s) are added while the multistage polymer is at or below the temperature at which the shell was polymerized, most preferably within ten degrees Celsius below the temperature at which the shell was polymerized.

Monomer which is present at, or after providing that no substantial polymerization of monomer is occurring can be (i) one or more of the monomers used to prepare any of the stages of the multistage polymer, (ii) one or more monomers other than those use to prepare any of the stages of the multistage polymer, or (iii) combinations thereof. Preferably, monomer present at such time is one or more of the monomers used to prepare the shell. Such monomer may be unreacted monomer from preparing the multi-stage emulsion polymer, it may be separately added, or a combination thereof. Preferably, the monomer is nonionic monomer. Nonionic monomer is preferred because acid-functional monomers will be neutralized by the swelling agent, and these neutralized monomers are difficult to remove by polymerization. Preferably the level of monomer present at, or after providing that no substantial polymerization of monomer is occurring is from 1 to 20 times as much as the standing monomer level during polymerization.

It is also necessary to use one or more swelling agents. Suitable swelling agents include, are those which, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core. Swelling agents may be aqueous or gaseous, volatile or fixed bases or combinations thereof.

Suitable swelling agents include volatile bases such as ammonia, ammonium hydroxide, and volatile lower aliphatic amines, such as morpholine, trimethylamine, and triethylamine, and the like; fixed or permanent bases such as potassium hydroxide, lithium hydroxide, zinc ammonium complex, copper ammonium complex, silver ammonium complex, strontium hydroxide, barium hydroxide and the like. Solvents, such as, for example, ethanol, hexanol, octanol, Texanol® solvent and those described in U.S. Pat. No. 4,594,363, may be added to aid in fixed or permanent base penetration. Ammonia and ammonium hydroxide are preferred.

When trying to maximize the extent of swelling, it is preferable that the one or more swelling agents are added after providing that no substantial polymerization of monomer is occurring. The amount of swelling agent can be less than, equal to or greater than the amount needed to provide for complete neutralization of the core. Preferably, the amount of swelling agent is in the range of from 75 to 300 percent, more preferably in the range of from 90 to 250 percent based on the equivalents of the functionality in the core capable of being neutralized. It is also preferable to add the one or more swelling agents to the multistage emulsion

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polymer while the multistage emulsion polymer is at an elevated temperature, preferably at a temperature within 10° C. of the shell polymerization temperature. Swelling is generally very efficient under conditions of elevated temperature, in the presence of monomer and no substantial polymerization occurring. Under these conditions, swelling is generally complete within 30 minutes, preferably within 20 minutes, most preferably within 10 minutes of adding the one or more swelling agents.

The core polymer of the multistage emulsion polymer swells when the core is subjected to a basic swelling agent that permeates the shell to at least partially neutralize the hydrophilic-functionality of the core, preferably to a pH of at least about 6 to at least about 10, and thereby result in swelling by hydration of the hydrophilic core polymer. The swelling, or expansion, of the core may involve partial merging of the outer periphery of the core into the pores of the inner periphery of the shell and also partial enlargement or bulging of the shell and the entire particle overall.

When the swollen multistage emulsion polymer is dried, water and/or swelling agent are removed from the central region of the swollen multistage emulsion polymer, the core tends to shrink and a void develops, the extent of which depends upon the resistance of the shell to restoration to its previous size. This resistance of the shell restoring itself to its previous size is critical for minimizing the dry bulk density of the swollen multistage emulsion polymer. The expansion of the core results in expansion of the shell also. As the size of the shell is restored to its previous size, the dry bulk density increases. It is desirable, therefore, to minimize the extent to which the size of the shell is restored, thereby maximizing the dry bulk density of the swollen multistage emulsion polymer.

This can be accomplished by reducing the monomer level. It is believed that the presence of monomer is helpful in facilitating the swelling of the multistage polymer, whether by plasticizing the shell, aiding in the transport through the shell or a combination thereof. However, the presence of monomer is detrimental when trying to maximize swelling and minimize the dry bulk density of the swollen multistage emulsion polymer. Accordingly, after swelling the multistage emulsion polymer in the presence of both monomer and swelling agent, it is desirable to reduce the level of monomer to less than 10,000 ppm, preferably to less than 5,000 ppm based on polymer solids. This can be accomplished by any suitable means. Preferably, the level of monomer is reduced by polymerizing the monomer. This can be accomplished by any suitable means, such as by adding one or more initiators such as those recited above. It is preferred to begin to reduce the level of monomer within 20 minutes, more preferably within 10 minutes, of adding the one or more swelling agents.

The process of the present invention is capable of producing swollen multi-stage emulsion polymers having very low bulk density. Swollen emulsion multi-stage polymers having an a particle size below 275 nm can be prepared with a dry bulk density of from 0.30 to 0.77 g/cc, preferably from 0.35 to 0.76 g/cc, most preferably from 0.40 to 0.75 g/cc. Swollen emulsion multi-stage polymers having an a particle size in the range of from 275 to 500 nm can be prepared with a dry bulk density of from 0.30 to 0.74 g/cc, preferably from 0.35 to 0.73 g/cc, most preferably from 0.40 to 0.72 g/cc. Swollen emulsion multi-stage polymers having an a particle size in the range of from 501 to 750 nm can be prepared with a dry bulk density of from 0.30 to 0.59 g/cc, preferably from 0.35 to 0.58 g/cc, most preferably from 0.40 to 0.57 g/cc. Swollen emulsion multi-stage polymers having an a particle

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size in the range of from 751 to 1,300 nm can be prepared with a dry bulk density of from 0.30 to 0.46 g/cc, preferably from 0.35 to 0.45 g/cc, most preferably from 0.40 to 0.44 g/cc.

When the swollen multistage emulsion polymers are at least partially dried to produce voided polymer particles, these voided polymer particles impart favorable properties, such as gloss, brightness and opacity to paper coating formulations to which they are added.

The voided latex particles produced by the method of the present invention are useful in coating compositions, such as aqueous-based paint and paper coatings. The voided polymer particles produced by the method of this invention impart improved gloss, brightness and opacity to paper coating formulations to which they are added. Also, the voided polymer particles produced by the method of this invention impart opacity to aqueous coating compositions, such as paints, to which they are added.

#### EXAMPLE 1

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.5 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 71.2 grams of SDS (23%) and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 10.4 grams of SDS (23%), and 20.5 grams of Plurafac® B-25-5 (Plurafac is a trademark of BASF), followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 30.3% solids content and an average particle size of 145 nm.

#### EXAMPLE 2

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.7 grams of Abex® CO-436 surfactant (Abex is a trademark of Rhone Poulenc), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 14.5 grams of Abex® CO-436, and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 1.40 grams of Abex® CO-436, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to

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25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 31.4% solids content and an average particle size of 146 nm.

## EXAMPLE 3

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.7 grams of Abex® CO-436 surfactant, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 27.0 grams of Abex® CO-436, and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 4.0 grams of Abex® CO-436, and 20.0 grams of Plurafac® B-25-5 followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.7, 31.9% solids content and an average particle size of 153 nm.

## EXAMPLE 4

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 80° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 335 grams of deionized water, 14.0 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 4.5 grams of methacrylic acid, and 364.5 grams of methyl methacrylate. From this ME, 82 grams were removed and set aside. To the remaining ME was added 7.0 grams of SDS (23%) and 241.0 grams of methacrylic acid. With the kettle water at 80° C., the ME removed from the initial ME was added to the kettle, followed by the addition of a mixture of 2.75 grams of sodium persulfate in 15 grams of deionized water. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 80° C. After the completion of the monomer feed the dispersion was held at 80° C. for 15 minutes, cooled to 250C and filtered to remove any coagulum. The filtered dispersion had a pH of 3.1, 22.1% solids content and an average particle size of 184 nm.

## EXAMPLE 5

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.7 grams of Abex® CO-436 surfactant, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 9.0 grams of Abex® CO-436, and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 0.90 grams of Abex® CO-436, followed by the ME removed

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from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water was added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 31.6% solids content and an average particle size of 171 nm.

## EXAMPLE 6

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 80° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 335 grams of deionized water, 10.7 grams of Disponil® Fes-993 surfactant (Disponil is a trademark of Henkel), 4.5 grams of methacrylic acid, and 364.5 grams of methyl methacrylate. From this ME, 82 grams were removed and set aside. To the remaining ME was added 5.40 grams of Disponil® Fes-993 and 241.0 grams of methacrylic acid. With the kettle water at 80° C., a mixture of 50 grams of deionized water and 10.0 grams of Plurafac® B- 25-5, followed by the ME removed from the initial ME, followed by a mixture of 2.75 grams of sodium persulfate in 15 grams of deionized water were added to the kettle. The reaction mixture was stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 80° C. After the completion of the monomer feed the dispersion was held at 80° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.1, 21.5% solids content and an average particle size of 161 nm.

## EXAMPLE 7

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 80° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 335 grams of deionized water, 14.0 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 4.5 grams of methacrylic acid, and 364.5 grams of methyl methacrylate. From this ME, 82 grams were removed and set aside. To the remaining ME was added 7.0 grams of SDS(23%) and 241.0 grams of methacrylic acid. With the kettle water at 80° C., a mixture of 50 grams of deionized water and 9.8 grams of Plurafac® B- 25-5, followed by the ME removed from the initial ME, followed by a mixture of 2.75 grams of sodium persulfate in 15 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 80° C. After the completion of the monomer feed the dispersion was held at 80° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 21.9% solids content and an average particle size of 220 nm.

## EXAMPLE 8

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion

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(ME) was prepared by mixing 720 grams of deionized water, 6.85 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 15.0 grams of SDS (23%) and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 1.75 grams of SDS (23%), and 10.0 grams of Plurafac® B-25-5, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.9, 31.9% solids content and an average particle size of 349 nm.

## EXAMPLE 9

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 5.25 grams of Disponil® Fes-993, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 11.5 grams of Disponil® Fes-993 and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 0.4 grams of Disponil® Fes-993, and 20.5 grams of Silwet® L-7001 (Silwet is a trademark of Witco), followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 31.6% solids content and an average particle size of 401 nm.

## EXAMPLE 10

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 80° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 335 grams of deionized water, 1.0 gram of Abex® CO-436, 4.5 grams of methacrylic acid, and 364.5 grams of methyl methacrylate. From this ME, 82 grams were removed and set aside. To the remaining ME was added 2.80 grams of Abex® CO-436 and 241.0 grams of methacrylic acid. With the kettle water at 80° C., the ME removed from the initial ME, followed by a mixture of 2.75 grams of ammonium persulfate in 15 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 80° C. After the completion of the monomer feed the dispersion was held at 80° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 22.2% solids content and an average particle size of 328 nm.

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## EXAMPLE 11

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.8 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 51.5 grams of SDS and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 25.0 grams of SDS, and 20.5 grams of Plurafac® B-25-5, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 31.6% solids content and an average particle size of 94 nm.

## EXAMPLE 12

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.8 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 51.5 grams of SDS and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 25.0 grams of SDS(23%), and 20.5 grams of Silwet® L-7210, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.9, 31.5% solids content and an average particle size of 81nm.

## EXAMPLE 13

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.65 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 62.6 grams of SDS(23%) and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 20.2 grams of SDS(23%), followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized

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water were added to the kettle. The reaction mixture was stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 250C and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 30.6% solids content and an average particle size of 91 nm.

EXAMPLE 14

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2260 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.70 grams of Abex® CO-436, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 23.0 grams of Abex® CO-436 and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 8.0 grams of Abex® CO-436, followed by he ME removed from the initial ME, followed by a mixture of 2.75 grams of ammonium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 28.7% solids content and an average particle size of 80 nm.

EXAMPLE 15

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 17.2 grams of Abex® CO-436, 520.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 3.0 grams of Abex® CO-436, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 30.7% solids content and a average particle size of 87 nm.

EXAMPLE 16

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.7 grams of Abex® CO-436, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 14.5 grams of Abex® CO-436, and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 3.0 grams of Abex® CO-436, followed by the ME removed from the

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initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 31.3% solids content and an average particle size of 118 nm.

The dry bulk density, as used herein, and in the appended claims, was determined according to the following procedure. To a 50 milliliter ("ml") centrifuge tube was added 6.3 grams of polymer solids. Deionized water was added to the centrifuge tube to provide a total of 35 grams ("g") of material in the centrifuge tube which corresponds to 18 percent by weight of polymer solids. The tube was placed in a centrifuge spun at 18,000 revolutions per minute for 120 minutes. The supernatant was decanted and weighed. The dry density was then determined by the following equations:

Dry Density = % Poly × d

% Poly = 1 - % H2O

$$\% H2O = \frac{V_{H2O}}{V_{H2O} + V_P} = \frac{(V_T - S_{H2O}) \times F_R - V_P}{(V_T - S_{H2O}) \times F_R}$$

$$V_{H2O} = (V_T - S_{H2O}) \times F_R - V_P$$

$$V_P + V_{H2O} = (V_T - S_{H2O}) \times F_R$$

$$F_R = \frac{V_P + V_{H2O}}{V_P + V_{H2O} + I_{H2O}} = \frac{V_P + V_{H2O}}{\text{Hard Pack}}$$

$$\text{Hard Pack} = V_T - S_{H2O} = \frac{V_P + V_{H2O}}{F_R}$$

where:

W<sub>T</sub>=total weight in tube=35.0 grams

V<sub>H2O</sub>=Volume of water inside the particles

I<sub>H2O</sub>=Interstitial water volume

d=polymer density=measured 1.084 g/cc

V<sub>P</sub>=Polymer volume (6.3 g/1.084 g/cc=5.81 cc)

V<sub>T</sub>=total volume in tube=35 g-6.3 g solids=28.7g or cc

water+5.81 cc polymer=34.51 cc

S<sub>H2O</sub>=volume of supemate=weight of supemate

%<sub>H2O</sub>=Percent water inside particles

% POLY=Percent polymer in particles

F<sub>R</sub>=Packing constant, which is a correction corresponding to the fraction of volume solids in the hard pack. The following packing constant values were used based on the particle size of the polymer sample:

Particle Size Range (nm)	F <sub>R</sub>
<275	0.611
275-500	0.624
501-750	0.638
751-1300	0.645

The values of the packing constants used were based on density determinations (as described above) for unswollen polymer particles such that V<sub>H2O</sub> is zero. The packing constant, F<sub>R</sub> is defined as:

$$F_R = \frac{V_P + V_{H2O}}{V_P + V_{H2O} + I_{H2O}} = \frac{V_P + V_{H2O}}{\text{Hard Pack}} = \frac{V_P}{\text{Hard Pack}}$$

V<sub>P</sub>=Polymer volume (6.3 g/1.084 g/cc=5.81 cc)



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$I_{H2O}$ =Interstitial water volume=( $W_T-S_{H2O}-6.3$  g)/1.0 g/cc

$W_T$ =total weight in tube=35.0 grams

$S_{HS}$ =weight of supemate

Using the above expression the packing constants were determined for several polymer samples having average particle sizes in the range of from about 200 nm to 1275 nm..

Sample #	P.S. (nm)	$S_{H2O}$	$V_P$	$I_{H2O}$	$V_P + I_{H2O}$	$F_R$
1	213	25.0	5.81	3.70	9.51	0.611
2	440	25.2	5.81	3.50	9.31	0.624
3	650	25.4	5.81	3.30	9.11	0.638
4	1275	25.5	5.81	3.20	9.01	0.645

All particle sizes reported herein were measured using a Brookhaven BI-90 Particle Sizer and are reported as an average particle size.

EXAMPLE 17

A 5-liter, four necked round bottom flask was equipped with paddle stirrer thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 190.5 grams of the core prepared in Example 1. A monomer emulsion (ME I) which was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS(23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From this ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.5%, a pH of 10.0, and a particle size of 404 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.6189 g/cc.

EXAMPLE 18

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium

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persulfate dissolved in 30 grams of deionized water. This was immediately followed by 191.0 grams of the core prepared in Example 2. A monomer emulsion (ME I) which was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%),10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.4%, a pH of 9.9, and a particle size of 440 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density was calculated to be 0.6077 g/cc.

EXAMPLE 19

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 3. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of M II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/ minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch is cooled to 85° C. When the contents of the reactor reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed.

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The final latex had a solids content of 27.3%, a pH of 10.2, and a particle size of 370 nm. An acid titration showed good core encapsulation with only 2.5% core acid titratable. The dry density was calculated to be 0.6466 g/cc.

## EXAMPLE 20

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1400 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 271.5 grams of the core prepared in Example 4. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 800.

Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From ME I, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the kettle is allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The contents of the reactor were held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 29.5%, a pH of 10.2, and a particle size of 525 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.5735 g/cc.

## EXAMPLE 21

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After

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10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.3%, a pH of 10.2, and a particle size of 577 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.5605 g/cc.

## EXAMPLE 22

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 279.9 grams of the core prepared in Example 6. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.6%, a pH of 10.1, and a particle size of 515 nm. An acid titration showed good core encapsulation with only 2.5% core acid titratable. The dry density of this polymer was determined to be 0.5979 g/cc.

## EXAMPLE 23

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium

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persulfate dissolved in 30 grams of deionized water. This was immediately followed by 274.0 grams of the core prepared in Example 7. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the batch was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.6%, a pH of 10.3, and a particle size of 650 nm. An acid titration showed good core encapsulation with only 5.4% core acid titratable. The dry density of this polymer was determined to be 0.5804 g/cc.

## EXAMPLE 24

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 8. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, and 1.5 grams of allyl methacrylate. From ME II, 114 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the temperature of the kettle reached 85° C., the held back portion of ME II (114 grams) was added to the reactor followed by the addition of 38 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The kettle was held for 30 minutes at 85°

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C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.6%, a pH of 10.4, and a particle size of 1235 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.4670 g/cc.

## EXAMPLE 25

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.9 grams of the core prepared in Example 9. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, 3.0 grams of linseed oil fatty acid and 1.5 grams of allyl methacrylate. From ME II, 114 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (114 grams) was added to the reactor followed by the addition of 38 grams of ammonium hydroxide. The contents of the kettle were held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The batch was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.4%, a pH of 10.3, and a particle size of 1275 nm. An acid titration showed good core encapsulation with only 4.5% core acid titratable. The dry density of this polymer was determined to be 0.4357 g/cc.

## EXAMPLE 26

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 270.3 grams of the core prepared in Example 10. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, and 3.0 grams of divinyl benzene. From ME II, 114

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grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (114 grams) was added to the reactor followed by the addition of 38 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.1%, a pH of 10.0, and a particle size of 907 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.4648 g/cc.

## EXAMPLE 27

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 11. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS(23%), and 720 grams of styrene. From ME I, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.0%, a pH of 10.2, and a particle size of 276 nm. An acid titration showed good core encapsulation with only 4.5% core acid titratable. The dry density of this polymer was determined to be 0.6985 g/cc.

## EXAMPLE 28

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux

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condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 190.5 grams of the core prepared in Example 12. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.0%, a pH of 10.2, and a particle size of 213 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.7631 g/cc.

## EXAMPLE 29

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 196.1 grams of the core prepared in Example 13. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, 720 grams of styrene, and 3.6 grams of linseed oil fatty acid. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor

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followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 24.9%, a pH of 10.2, and a particle size of 284 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.6500 g/cc.

## EXAMPLE 30

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1620 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 2.66 grams of sodium persulfate dissolved in 21.0 grams of deionized water. This was immediately followed by 146.3 grams of the core prepared in Example 14. A monomer emulsion (ME I) was prepared by mixing 70 grams of deionized water, 4.2 grams of SDS, 15.1 grams of butyl methacrylate, 149.5 grams of methyl methacrylate, and 3.36 grams of methacrylic acid and was added to the kettle at a rate of 4.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 133 grams of deionized water, 2.7 grams of SDS, and 504 grams of styrene. From ME II, 64 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 8.8 grams/minute and a mixture of 1.3 grams of sodium persulfate dissolved in 60 grams of deionized water was co-fed to the reactor at a rate of 1.50 grams/minute. After 10 minutes the rate of ME II was increased to 17.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 5.6 grams of 4-hydroxy TEMPO and 5.6 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reaches 85° C., the held back portion of ME II (64.0 grams) was added to the reactor followed by the addition of 26.6 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.67 grams of sodium persulfate dissolved in 14 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 24.5%, a pH of 10.2, and a particle size of 196 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.7955 g/cc.

## EXAMPLE 31

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 195.4 grams of the core prepared in Example 15. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a

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temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reaches 85° C., the held back portion of ME II (137.0 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.2%, a pH of 10.0, and a particle size of 305 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.6690 g/cc.

## EXAMPLE 32

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 191.5 grams of the core prepared in Example 16. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), 720 grams of styrene, and 3.6 grams of divinyl benzene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the batch was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137.0 grams) was added to the kettle followed by the addition of 42 grams of ammonium hydroxide. The kettle temperature was held at 85° C. for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.4%, a pH of 10.2, and a particle size of 334 nm. An acid titration showed good core encapsulation with only 2.5% core acid titratable. The dry density of this polymer was determined to be 0.6445 g/cc.

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## EXAMPLE 33

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 199.8 grams of the core prepared in Example 1. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the batch was allowed to increase to 92° C. Upon completion of the ME II and co-feeds the batch was cooled to 85° C. (no inhibitor added). When the kettle temperature reached 85° C., the held back portion of ME II (137.0 grams) was added to the kettle followed by the addition of 42 grams of ammonium hydroxide. The kettle temperature was held at 85° C. for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.5%, a pH of 10.1, and a particle size of 320 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.7818 g/cc.

## EXAMPLE 34

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 199.8 grams of the core prepared in Example 1. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. The ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the batch was allowed to increase to 92° C. When 777 grams of the ME II had been added to the kettle, 42 grams of ammonium hydroxide were added to the kettle and the ME II was continued. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92° C. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was

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added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.7%, a pH of 10.1, and a particle size of 406 nm. An acid titration showed more core acid titratable (8.7%) compared to example #17. The dry density of this polymer was determined to be 0.6906 g/cc.

## EXAMPLE 35

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 199.8 grams of the core prepared in Example 1. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. The ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the batch was allowed to increase to 92° C. When 457 grams of the ME II had been added to the kettle, 42 grams of ammonium hydroxide were added to the kettle and the ME II was continued. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92° C. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 24.0%, a pH of 10.0, and a particle size of 573 nm which was an increase in particle size over Example 17 (404 nm); some aggregation of the particles was observed which may account for the increased particle size measured. The increased particle size is an indication of particle aggregation caused by an increase in the amount of core acid in the aqueous phase and indeed an acid titration showed high core acid titratable (14.4%) compared to example #17. The dry density of this polymer was determined to be 0.6367 g/cc.

## EXAMPLE 36

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams

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of styrene. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. When 777 grams of ME II had been fed to the kettle, 42 grams of ammonium hydroxide were then added to the kettle. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 920. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.8%, a pH of 10.2, and a particle size of 570 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.6364 g/cc.

## EXAMPLE 37

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 800. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. When 457 grams of ME II had been fed to the kettle, 42 grams of ammonium hydroxide were then added to the kettle. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 920. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.5%, a pH of 10.2, and a particle size of 725 nm which was an increase in particle size over Example 21 (577 nm). The increased particle size is an indication of particle aggregation caused by an increase in the amount of core acid in the aqueous phase and indeed an acid titration showed high core acid titratable (18.5%) compared to Example 21. The dry density of this polymer was determined to be 0.6284 g/cc.

## EXAMPLE 38

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams

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of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. When the ME II and co-feeds were complete, 42 grams of ammonium hydroxide were then added to the kettle. The batch was held for 5 minutes at 92°. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.3%, a pH of 10.3, and a particle size of 530 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.8220 g/cc.

## EXAMPLE 39

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2A grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 1 gram of N, N-diethylhydroxylamine and 16 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.0%, a pH of 10.2, and a particle size of 580 nm. An acid



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titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.5574 g/cc.

## EXAMPLE 40

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds, 42 grams of a 1% solution of 4-nitrosophenol magnesium salt in water was added to the contents of the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.8%, a pH of 10.2, and a particle size of 585 nm. An acid titration showed good core encapsulation with only 5.4% core acid titratable. The dry density of this polymer was determined to be 0.5481 g/cc.

## EXAMPLE 41

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 8. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, and 1.5 grams of allyl methacrylate. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was

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increased to 25 grams/minute. The temperature of kettle was allowed to increase to 92° C. When 650 grams of ME II had been fed to the kettle, 38 grams of ammonium hydroxide were added to the kettle. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92° C. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The kettle was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.9%, a pH of 10.3, and a particle size of 976 nm. An acid titration showed good core encapsulation with only 4.4% core acid titratable. The dry density of this polymer was determined to be 0.5247 g/cc.

## EXAMPLE 42

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 8. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, and 1.5 grams of allyl methacrylate. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of kettle was allowed to increase to 92° C. When the ME II and co-feeds had been completed, 38 grams of ammonium hydroxide were added to the kettle and the batch was held for 5 minutes. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The kettle was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.9%, a pH of 10.2, and a particle size of 1023 nm. An acid titration showed good core encapsulation with only 2.7% core acid titratable. The dry density of this polymer was determined to be 0.6945 g/cc.

## EXAMPLE 43

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 195.4 grams of the core prepared in Example 15. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing



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190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. The ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds, 42 grams of ammonium hydroxide were added to the kettle and the batch was held at 92° C. for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.5%, a pH of 10.2, and a particle size of 232 nm. An acid titration showed good core encapsulation with only 6.4% core acid titratable. The dry density of this polymer was determined to be 0.9115 g/cc.

## EXAMPLE 44

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 195.4 grams of the core prepared in Example 15. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. The ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. When 777 grams of ME II had been added to the kettle, 42 grams of ammonium hydroxide were added to the kettle. Upon completion of the ME II and co-feeds, the batch was held at 920C for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.2%, a pH of 10.2, and a particle size of 268 nm. An acid titration showed fair core encapsulation with 7.2% core acid titratable. The dry density of this polymer was determined to be 0.7688 g/cc.

## EXAMPLE 45

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 196.1 grams of the core prepared in Example 13. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams

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of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, 720 grams of styrene, and 1.8 grams of allyl methacrylate. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.6%, a pH of 10.1, and a particle size of 237 nm. An acid titration showed good core encapsulation with only 2.9% core acid titratable. The dry density of this polymer was determined to be 0.6868 g/cc.

## EXAMPLE 46

(Comparative) A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 11. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. When 822 grams of ME II had been added to the kettle, 42 grams of ammonium hydroxide were added to the contents of the kettle. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.1%, a pH of 10.2, and a particle size of 270 nm. An acid titration showed good core encapsulation with only 3.0% core acid titratable. The dry density of this polymer was determined to be 0.7746 g/cc.

## EXAMPLE 47

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux

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condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 191.5 grams of the core  
5 prepared in Example 16. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute  
10 at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9  
15 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the batch was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy  
20 TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137.0 grams) was added to the kettle followed by the addition of 42 grams of ammonium hydroxide. The kettle temperature was held at 85° C. for 5 minutes. After the 5  
25 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.5%, a pH of 10.2, and a particle size of 385  
30 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.6226 g/cc.

## EXAMPLE 48

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux  
40 condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 271.5 grams of the core  
45 prepared in Example 4. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute  
50 at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9  
55 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the kettle is allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8  
60 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42  
65 grams of ammonium hydroxide. The contents of the reactor

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were held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then  
5 cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.6%, a pH of 10.0, and a particle size of 525 nm. An acid titration showed good core encapsulation with only 4.4% core acid titratable. The dry density of this polymer was determined to be 0.5979 g/cc.

## EXAMPLE 49

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux  
condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core  
prepared in Example 8. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and  
was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second  
monomer emulsion (ME II) was prepared by mixing 136 grams of deionized water, 2.7 grams of SDS, 406.5 grams of styrene, 102 grams of acrylonitrile, and 1.5 grams of allyl  
methacrylate. A third monomer emulsion (ME III) was prepared by mixing 24 grams of deionized water, 0.5 grams of SDS, 0.2 grams of allyl methacrylate, and 90 grams of styrene. The initial portion of ME II was added to the kettle  
at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized  
water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25  
grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and  
co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8  
grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the temperature of the kettle reached 85° C., ME III was added to the reactor  
followed by the addition of 38 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After  
the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was  
added to the kettle. The kettle was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to  
remove any coagulum formed. The final latex had a solids content of 22.5%, a pH of 10.1, and a particle size of 906  
nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this  
polymer was determined to be 0.4539 g/cc.

We claim:

1. A process for preparing emulsion polymer particles comprising:

(a) providing an aqueous emulsion of

(i) multi-stage emulsion polymer, comprising a core stage polymer and a shell stage polymer, wherein the core stage polymer comprises, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core stage polymer, of hydrophilic monoethylenically unsaturated monomer, and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer; and

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wherein the shell stage polymer comprises, as polymerized units, at least 50 percent by weight of nonionic monoethylenically unsaturated monomer;

- (ii) monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer; and
  - (iii) swelling agent under conditions wherein there is no substantial polymerization of the monomer; and
- (b) reducing the level of monomer by at least fifty percent.

2. The process of claim 1 wherein the monomer at a level of at least 0.5 percent by weight based on the weight of the

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multi-stage emulsion polymer is one or more of the monomers used to prepare the multi-stage emulsion polymer.

3. The process of claim 1 wherein the monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer is nonionic monomer.

4. The process of claim 1 wherein the swelling agent is selected from volatile base, fixed base, and combinations thereof.

5. The process of claim 1 wherein the level of monomer is reduced to less than 10,000 ppm based on polymer solids by polymerizing said monomer.

\* \* \* \* \*



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**Blankenship et al.**

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(54) **PROCESS FOR PREPARING MULTI-STAGE  
POLYMER EMULSIONS AND MULTI-STAGE  
POLYMERS FORMED THEREFROM**

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(58) **Field of Search** ..... **525/309, 244,**  
**525/301, 264, 263, 902, 255, 259, 256**

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(57) **ABSTRACT**

A process for preparing emulsion polymer particles comprising: (a) providing an aqueous emulsion of a multistage core-shell polymer with a hydrophilic core, (b) adding one or more inhibitors to substantially stop any polymerization, (c) adding monomer to the emulsion polymer, (d) adding swelling agent and (e) reducing the level of monomer by at least fifty percent. The process produces multistage polymers having low dry-bulk density useful in coating compositions such as paints and paper coatings.

**7 Claims, No Drawings**

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# PROCESS FOR PREPARING MULTI-STAGE POLYMER EMULSIONS AND MULTI-STAGE POLYMERS FORMED THEREFROM

This application is a divisional application of patent application Ser. No. 08/974,763, filed Nov. 20, 1997, now U.S. Pat. No. 6,020,435 and claims benefit to U.S. Provisional application Ser. No. 60/064,513 filed Nov. 5, 1997.

The present invention relates to processes for preparing polymer emulsions and polymers formed therefrom. In particular, the present invention relates to aqueous emulsion polymerization processes for preparing polymer emulsions and emulsion polymers formed therefrom.

"Emulsion polymer", as used herein, refers to a water-insoluble polymer which is prepared by emulsion polymerization techniques.

"Polymer emulsion", as used herein, refers to an aqueous composition having discrete, water-insoluble polymer particles dispersed therein.

As used herein, acrylate and methacrylate are referred to as "(meth)acrylate," acrylic acid and methacrylic acid are referred to as "(meth)acrylic acid."

Emulsion polymers, such as hollow or voided emulsion polymers, are known for use in several industrial applications. The literature uses the terms "hollow" and "voided" interchangeably. These polymers are often used in paints, coatings, inks, sunscreens and paper manufacture. Hollow emulsion polymers are generally prepared by swelling a core/shell emulsion polymer in such a way that one or more voids form in the interior of the emulsion polymer particle. These voids contribute, among other things, to the opacity of coatings and films prepared with the hollow emulsion polymer.

For some applications, it is particularly desirable to minimize the weight of the coating applied. For example, it is desirable for certain paper coatings applications to have a high performance coating without adding considerably to the weight of the paper.

Accordingly, it is desirable to provide lightweight, low density additives for coatings, such as voided latex particles.

Voided latex particles can be prepared by any of several known process, including those described U.S. Pat. Nos. 4,427,836, 4,468,498, 4,594,363, 4,880,842, 5,494,971, 5,521,253, 5,157,084, 5,360,827 among others. Voided latex particles, as described in the references noted above, are prepared by swelling the core of a core-shell emulsion polymer. Some of the processes, such as that described by U.S. Pat. No. 5,360,827 describe the processes whereby, in the latter stages of polymerizing the shell, monomer is added to facilitate diffusion of base into the core of the polymer in order to achieve swelling. Then, the pH of the emulsion is adjusted with a carboxyl-group containing monomer which is subsequently polymerized. However, this process is time consuming and does not result in suitable lightweight emulsion polymers.

The present invention seeks to overcome the deficiencies in the previously known processes by providing low density voided emulsion polymers and a process for preparing them.

In a first aspect of the present invention, there is provided a process for preparing emulsion polymer particles comprising:

- a) providing an aqueous emulsion of
  - i) multi-stage emulsion polymer, comprising a core stage polymer and a shell stage polymer, wherein the core stage polymer comprises, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core stage polymer, of

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hydrophilic monoethylenically unsaturated monomer, and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer; and

wherein the shell stage polymer comprises, as polymerized units, at least 50 percent by weight of nonionic monoethylenically unsaturated monomer;

ii) monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer; and

iii) swelling agent under conditions wherein there is no substantial polymerization of the monomer; and

b) reducing the level of monomer by at least fifty percent.

In a second aspect of the present invention, there is provided an aqueous polymer emulsion comprising water and swollen multi-stage emulsion polymer wherein the dry bulk density of the swollen multi-stage emulsion is: less than 0.77 grams per cubic centimeter ("g/cc") when the swollen multi-stage emulsion polymer has a particle size below 275 nanometers ("nm"); less than 0.74 g/cc when the swollen multi-stage emulsion polymer has a particle size of from 275 to 500 nm; less than 0.59 g/cc when the swollen multi-stage emulsion polymer has a particle size of from 501 to 750 nm; less than 0.46 g/cc when the swollen multi-stage emulsion polymer has a particle size of from 751 to 1300 nm.

The stages of the multi-stage polymers of the present invention include core stage polymer (the "core"), and shell stage polymer (the "shell"). The core and shell may themselves be comprised of more than one stage. There may also be one or more intermediate stages. Preferably, the multi-stage polymer comprises a core, an intermediate layer and a shell.

The cores of the multi-stage polymers of the present invention are emulsion polymers comprising, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core, of at least one hydrophilic monoethylenically unsaturated monomer and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer.

Cores containing at least five percent by weight, based on the total weight of the core polymer, of at least one hydrophilic monoethylenically unsaturated monomer will generally result in a suitable degree of swelling. There may be instances wherein, because of the hydrophobicity of certain comonomers or combinations thereof in conjunction with the hydrophobic/hydrophilic balance of a particular hydrophilic monomer, the copolymer may be suitably prepared with less than five percent by weight, based on the total weight of the core polymer, of a hydrophilic monoethylenically unsaturated monomer. Preferably, the core comprises, as polymerized units, hydrophilic monoethylenically unsaturated monomer at a level of from 5 to 100, more preferably, from 20 to 60, and most preferably, from 30 to 50 percent by weight based on the total weight of the core. The hydrophilic core polymer may be made in a single stage or step of the sequential polymerization or may be made by a plurality of steps in sequence.

The multi-stage emulsion polymer of the present invention contemplates a core polymer wherein at least one hydrophilic monoethylenically unsaturated monomer is polymerized alone or with at least one nonionic monoethylenically unsaturated monomer. This process also contemplates, and includes in the term "hydrophilic monoethylenically unsaturated monomer," the use of a nonpolymeric compound containing at least one carboxylic acid

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group which absorbed into the core polymer before, during or after the polymerization of the hydrophobic shell polymer as a replacement for the hydrophilic monoethylenically unsaturated monomer in the hydrophilic core polymer, as described in U.S. Pat. No. 4,880,842. In addition, this invention contemplates, and includes in the term "hydrophilic monoethylenically unsaturated monomer," the use of a latent hydrophilic core polymer which contains no hydrophilic monoethylenically unsaturated monomer but which is swellable upon hydrolysis to a hydrophilic core polymer as described in U.S. Pat. No. 5,157,084.

Suitable hydrophilic monoethylenically unsaturated monomer useful for making the core polymer include monoethylenically unsaturated monomers containing acid-functionality such as monomers containing at least one carboxylic acid group including acrylic acid, methacrylic acid, acryloxypropionic acid, (meth)acryloxypropionic acid, itaconic acid, aconitic acid, maleic acid or anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, monomethyl itaconate and the like. Acrylic acid and methacrylic acid are preferred.

Suitable nonpolymeric compounds containing at least one carboxylic acid group include  $C_6$ - $C_{12}$  aliphatic or aromatic monocarboxylic acids and dicarboxylic acids, such as benzoic acid, m-toluic acid, p-chlorobenzoic acid, o-acetoxybenzoic acid, azelaic acid, sebacic acid, octanoic acid, cyclohexanecarboxylic acid, lauric acid and monobutyl phthalate and the like.

Suitable nonionic monoethylenically unsaturated monomers for making the hydrophilic core polymer include styrene,  $\alpha$ -methyl styrene, p-methyl styrene, t-butyl styrene, vinyltoluene, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, (meth)acrylonitrile, (meth)acrylamide, ( $C_1$ - $C_{20}$ ) alkyl or ( $C_3$ - $C_{20}$ ) alkenyl esters of (meth)acrylic acid, such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate and the like.

The core, whether obtained by a single stage process or a process involving several stages, has an average particle size of from 50 nm to 1.0 micron, preferably from 100 nm to 300 nm, diameter in unswollen condition. If the core is obtained from a seed polymer, the seed polymer preferably has an average particle size of from 30 nm to 200 nm.

The core may also optionally contain less than 20 percent by weight, preferably from 0.1 to 3 percent by weight, based on the total weight of the core, of polyethylenically unsaturated monomer, wherein the amount used is generally approximately directly proportional to the amount of hydrophilic monoethylenically unsaturated monomer used; in other words, as the relative amount of hydrophilic monomer increases, it is acceptable to increase the level of polyethylenically unsaturated monomer. Alternatively, the core polymer may contain from 0.1 to 60 percent by weight, based on the total weight of the core polymer, of butadiene.

Suitable polyethylenically unsaturated monomers include comonomers containing at least two addition polymerizable vinylidene groups and are alpha beta ethylenically unsaturated monocarboxylic acid esters of polyhydric alcohols containing 2-6 ester groups. Such comonomers include alkylene glycol diacrylates and dimethacrylates, such as for example, ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate propylene glycol diacrylate and triethylene glycol dimethylacrylate; 1,3-glycerol dimethacrylate; 1,1,1-

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trimethylol propane dimethacrylate; 1,1,1-trimethylol ethane diacrylate; pentaerythritol trimethacrylate; 1,2,6-hexane triacrylate; sorbitol pentamethacrylate; methylene bis-acrylamide, methylene bis-methacrylamide, divinyl benzene, vinyl methacrylate, vinyl crotonate, vinyl acrylate, vinyl acetylene, trivinyl benzene, triallyl cyanurate, divinyl acetylene, divinyl ethane, divinyl sulfide, divinyl ether, divinyl sulfone, diallyl cyanamide, ethylene glycol divinyl ether, diallyl phthalate, divinyl dimethyl silane, glycerol trivinyl ether, divinyl adipate; dicyclopentenyl (meth)acrylates; dicyclopentenyl (meth)acrylates; unsaturated esters of glycol monodicyclopentenyl ethers; allyl esters of  $\alpha,\beta$ -unsaturated mono- and dicarboxylic acids having terminal ethylenic unsaturation including allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl itaconate and the like.

The multi-stage polymer of the present invention preferably contains an intermediate stage. The intermediate stage polymer, when present, partially or fully encapsulates the core and itself is partially or fully encapsulated by the shell. The intermediate stage is prepared by conducting an emulsion polymerization in the presence of the core.

The intermediate stage preferably contains, as polymerized units, from 0.3 to 20, more preferably from 0.5 to 10 percent by weight, based on the weight of the core, of at least one hydrophilic monoethylenically unsaturated monomer. The intermediate stage preferably contains, as polymerized units, from 80 to 99.7, more preferably from 90 to 99.5 percent by weight, based on the weight of the intermediate stage, of at least one nonionic monoethylenically unsaturated monomer. The hydrophilic monoethylenically unsaturated monomers and the nonionic monoethylenically unsaturated monomers useful for making the core are also useful for making the intermediate layer.

The shell of the multi-staged polymer of this invention is the product of emulsion polymerizing from 80 to 100, preferably from 90 to 100, percent by weight, based on the total weight of the shell, of at least one nonionic monoethylenically unsaturated monomer. The nonionic monoethylenically unsaturated monomers suitable for the core are also suitable for the shell. Styrene is preferred.

The shell may also contain, as polymerized units, from 0 to 20, preferably from 0 to 10, percent by weight based on the weight of the shell, of one or more monoethylenically unsaturated monomers containing acid-functionality for making the hydrophobic polymer shell include acrylic acid, methacrylic acid, acryloxypropionic acid, (meth)acryloxypropionic acid, itaconic acid, aconitic acid, maleic acid, maleic anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, monomethyl itaconate and the like. Acrylic acid and methacrylic acid are preferred.

The monomers used and the relative proportions thereof in the shell should be such that it is permeable to an aqueous or gaseous volatile or fixed basic swelling agent capable of swelling the core. Monomeric mixtures for making the shell preferably contain from about 0.1% by weight to about 10% by weight, based on the total weight of the shell polymer, of an acid-functional monoethylenically unsaturated monomer. Preferably, the proportion of acid-functional monoethylenically unsaturated monomer in the shell polymer does not exceed one-third the proportion thereof in the core polymer.

The presence of acid-functional monoethylenically unsaturated monomer in the shell polymer may serve several functions:

- (1) stabilizing of the final multi-stage emulsion polymer;
- (2) assuring permeability of the shell to a swelling agent; and

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(3) compatibilizing the shell with the previously formed stage of the multistage emulsion polymer.

As used herein, the term "sequentially emulsion polymerized" or "sequentially emulsion produced" refers to polymers (including homopolymers and copolymers) which are prepared in aqueous medium by an emulsion polymerization process in the presence of the dispersed polymer particles of a previously formed emulsion polymer such that the previously formed emulsion polymers are increased in size by deposition thereon of emulsion polymerized product of one or more successive monomer charges introduced into the medium containing the dispersed particles of the preformed emulsion polymer.

In the sequential emulsion polymerization with which the present invention is concerned, the term "seed" polymer is used to refer to an aqueous emulsion polymer dispersion which may be the initially-formed dispersion, that is, the product of a single stage of emulsion polymerization or it may be the emulsion polymer dispersion obtained at the end of any subsequent stage except the final stage of the sequential polymerization. Thus, a hydrophilic core polymer which is herein intended to be encapsulated by one or more subsequent stages of emulsion polymerization may itself be termed a seed polymer for the next stage.

The method of this invention contemplates that the core, the intermediate stage, the shell, or any combination thereof may be made in a single stage or step of the sequential polymerization or may be made by a plurality of steps in sequence following the polymerization. The first stage of emulsion polymerization in the process of the present invention may be the preparation of a seed polymer containing small dispersed polymer particles insoluble in the aqueous emulsion polymerization medium. This seed polymer may or may not contain any hydrophilic monomer component but provides particles of minute size which form the nuclei on which the hydrophilic core polymer, with or without non-ionic comonomer, is formed.

A water-soluble free radical initiator is utilized in the aqueous emulsion polymerization. Suitable water-soluble free radical initiators include hydrogen peroxide; tert-butyl peroxide; alkali metal persulfates such as sodium, potassium and lithium persulfate; ammonium persulfate; and mixtures of such initiators with a reducing agent. Reducing agents include: sulfites, such as alkali metal metabisulfite, hydrosulfite, and hyposulfite; sodium formaldehyde sulfoxylate; and reducing sugars such as ascorbic acid and isoascorbic acid. The amount of initiator is preferably from 0.01 to 3 percent by weight, based on the total amount of monomer and in a redox system the amount of reducing agent is preferably from 0.01 to 3 percent by weight based on the total amount of monomer. The temperature may be in the range of about 10° C. to 100° C. In the case of the persulfate systems, the temperature is preferably in the range of 60° C. to 90° C. In the redox system, the temperature is preferably in the range of 30° C. to 70° C., preferably below about 60° C., more preferably in the range of 30° C. to 45° C. The type and amount of initiator may be the same or different in the various stages of the multi-stage polymerization.

One or more nonionic or anionic emulsifiers, or surfactants, may be used, either alone or together. Examples of suitable nonionic emulsifiers include tert-octylphenoxyethylpoly(39)-ethoxyethanol, dodecylpoly(10)ethoxyethanol, nonylphenoxyethyl-poly(40)ethoxyethanol, polyethylene glycol 2000 monooleate, ethoxylated castor oil, fluorinated alkyl esters and alkoxyates, polyoxyethylene (20) sorbitan monolaurate,

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sucrose monocoate, di(2-butyl)phenoxypoly(20)ethoxyethanol, hydroxyethylcellulosepolybutyl acrylate graft copolymer, dimethyl silicone polyalkylene oxide graft copolymer, poly(ethylene oxide)poly(butyl acrylate) block copolymer, block copolymers of propylene oxide and ethylene oxide, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylated with 30 moles of ethylene oxide, N-polyoxyethylene (20)lauramide, N-lauryl-N-polyoxyethylene(3)amine and poly(10)ethylene glycol dodecyl thioether. Examples of suitable anionic emulsifiers include sodium lauryl sulfate, sodium dodecylbenzenesulfonate, potassium stearate, sodium dioctyl sulfosuccinate, sodium dodecylphenyloxide disulfonate, nonylphenoxyethylpoly(1)ethoxyethyl sulfate ammonium salt, sodium styrene sulfonate, sodium dodecyl allyl sulfosuccinate, linseed oil fatty acid, sodium or ammonium salts of phosphate esters of ethoxylated nonylphenol, sodium octoxynol-3-sulfonate, sodium cocoyl sarcosinate, sodium 1-alkoxy-2-hydroxypropyl sulfonate, sodium alpha-olefin (C<sub>14</sub>-C<sub>16</sub>)sulfonate, sulfates of hydroxyalkanols, tetrasodium N-(1,2-dicarboxy ethyl)-N-octadecylsulfosuccinate, disodium N-octadecylsulfosuccinate, disodium alkylamido polyethoxy sulfosuccinate, disodium ethoxylated nonylphenol half ester of sulfosuccinic acid and the sodium salt of tert-octylphenoxyethoxypoly(39)ethoxyethyl sulfate. The one or more surfactants are generally used at a level of from 0 to 3 percent based on the weight of the multi-stage polymer. The one or more surfactants can be added prior to the addition of any monomer charge, during the addition of a monomer charge or a combination thereof. In certain monomer/emulsifier systems for forming the shell, the tendency to produce gum or coagulum in the reaction medium may be reduced or prevented by the addition of about 0.05% to about 2.0% by weight, based on total weight of the shell polymer, of emulsifier without detriment to the deposition of the polymer formed on the previously formed core particles.

The amount of emulsifier may be zero, in the situation wherein a persulfate initiator is used, to 3 percent by weight, based on the weight of total weight of the core polymer. By carrying out the emulsion polymerization while maintaining low levels of emulsifier, the subsequent stages of polymerization deposit the most-recently formed polymer on the existing dispersed polymer particles resulting from the preceding step or stage. As a general rule, the amount of emulsifier should be kept below that corresponding to the critical micelle concentration for a particular monomer system, but while this limitation is preferable and produces a unimodal product, it has been found that in some systems the critical micelle concentration of the emulsifier may be exceeded somewhat without the formation of an objectionable or excessive number of dispersed micelles or particles. It is for the purpose of controlling the number of micelles during the various stages of polymerization so that the deposition of the subsequently formed polymer in each stage occurs upon the dispersed micelles or particles formed in the previous stages, that the concentration of emulsifier is kept low.

The viscosity—average molecular weight of the polymer formed in a given stage may range from 100,000, or lower if a chain transfer agent is used, to several million molecular weight. When 0.1% by weight to 20% by weight, based on the weight of the monomer, of a polyethylenically unsaturated monomer mentioned hereinbefore is used in making the core, the molecular weight is increased whether or not crosslinking occurs. The use of the polyethylenically unsaturated monomer reduces the tendency of the core polymer to dissolve when the multistaged polymer is treated with a

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swellant for the core. If it is desired to produce a core having a molecular weight in the lower part of the range, such as from 500,000 down to as low as about 20,000, it is frequently most practical to do so by avoiding the polyethylenically unsaturated monomers and using a chain transfer agent instead, such as 0.05% to 2% or more thereof, examples being alkyl mercaptans, such as sec-butyl mercaptan.

The weight ratio of core to the intermediate stage, if present, is generally in the range of from 1:0.5 to 1:10, preferably in the range of from 1:1 to 1:7. The weight ratio of core to shell is generally in the range of from 1:5 to 1:20, preferably in the range of from 1:8 to 1:15. When trying to decrease the dry density of the final product, is preferred to have as little shell as possible while still encapsulating the core.

The amount of polymer deposited to form shell polymer is generally such as to provide an overall size of the multistage polymer particle of from 70 nm to 4.5 microns, preferably from 100 nm to 3.5 microns, more preferably from 200 nm to 2.0 microns, in unswollen condition (that is, before any neutralization to raise the pH to about 6 or higher) whether the shell polymer is formed in a single stage or in a plurality of stages. In order to minimize the dry density of the final product, it is preferable to deposit only as much shell polymer as is needed to fully encapsulate the core. When the hydrophilic core polymer is fully encapsulated, it does not titrate with alkali metal bases under normal analytical conditions of about 1 hour and at room temperature. The extent of encapsulation can be determined by removing samples during the course of the shell polymerization and titrating with sodium hydroxide.

The multi-stage emulsion polymer is prepared by sequential emulsion polymerization, which, as discussed above, includes charging the monomers which form the shell. At, or near, the conclusion of charging the monomers which form the shell, the contents of the reactor include the multistage polymer, water and unreacted monomer. Under the conditions of an emulsion polymerization, there is also an appreciable free-radical content, or radical flux, which keeps the polymerization process going. Even if no additional monomer or initiator is added, there is an appreciable free-radical content in the system. When there is no appreciable free-radical content, in other words, when the radical flux is very low or approaches zero, then no substantial amount of polymerization will occur.

We have discovered that this free-radical content interferes with the extent of swelling which can be achieved. Previously known processes typically achieve swelling by adding a suitable swelling agent in the latter stages of charging the monomers which form the shell or at the completion of charging the monomers which form the shell. It is believed that the presence of unreacted monomer facilitates the transport of the swelling agent to the core. However, in previously known processes, the swelling agent was added to the system while there was still an appreciable free-radical content in the system. Thus, under those conditions, a substantial amount of polymerization was still occurring.

We have discovered that by providing an aqueous emulsion of the multi-stage emulsion polymer, monomer and swelling agent under conditions wherein there is no substantial polymerization of the monomer, we can enhance the extent of swelling of the multistage emulsion polymer.

There are many means for providing that no substantial polymerization of monomer is occurring, including the addition of one or more polymerization inhibitors, the addi-

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tion of one or more reducing agents, waiting for a sufficient period of time until there are no longer an appreciable number of free-radicals by virtue of them terminating, cooling the contents of the reactor to limit the reactivity of the free-radicals, and combinations thereof. A preferred means involves the addition of one or more polymerization inhibitors such as, for example, N,N-diethylhydroxylamine, N-nitrosodiphenylamine, 2,4-dinitrophenylhydrazine, p-phenylenediamine, phenathiazine, alloocimene, triethyl phosphite, 4-nitrosophenol, 2-nitrophenol, p-aminophenol, 4-hydroxy-TEMPO (also known as 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy, free radical), hydroquinone, p-methoxyhydroquinone, tert-butyl-p-hydroquinone, 2,5-di-tert-butyl-p-hydroquinone, 1,4-naphthalenediol, 4-tert butyl catechol, copper sulfate, copper nitrate, cresol and phenol. When used, the polymerization inhibitors or reducing agents are added in effective amount to substantially stop any polymerization, generally from 25 to 5,000 parts per million ("ppm"), preferably from 50 to 3,500 ppm based on polymer solids. Preferably, the polymerization inhibitor(s) or reducing agent(s) are added while the multistage polymer is at or below the temperature at which the shell was polymerized, most preferably within ten degrees Celsius below the temperature at which the shell was polymerized.

Monomer which is present at, or after providing that no substantial polymerization of monomer is occurring can be (i) one or more of the monomers used to prepare any of the stages of the multistage polymer, (ii) one or more monomers other than those used to prepare any of the stages of the multistage polymer, or (iii) combinations thereof. Preferably, monomer present at such time is one or more of the monomers used to prepare the shell. Such monomer may be unreacted monomer from preparing the multi-stage emulsion polymer, it may be separately added, or a combination thereof. Preferably, the monomer is nonionic monomer. Nonionic monomer is preferred because acid-functional monomers will be neutralized by the swelling agent, and these neutralized monomers are difficult to remove by polymerization. Preferably the level of monomer present at, or after providing that no substantial polymerization of monomer is occurring is from 1 to 20 times as much as the standing monomer level during polymerization.

It is also necessary to use one or more swelling agents. Suitable swelling agents include, are those which, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core. Swelling agents may be aqueous or gaseous, volatile or fixed bases or combinations thereof.

Suitable swelling agents include volatile bases such as ammonia, ammonium hydroxide, and volatile lower aliphatic amines, such as morpholine, trimethylamine, and triethylamine, and the like; fixed or permanent bases such as potassium hydroxide, lithium hydroxide, zinc ammonium complex, copper ammonium complex, silver ammonium complex, strontium hydroxide, barium hydroxide and the like. Solvents, such as, for example, ethanol, hexanol, octanol, Texanol® solvent and those described in U.S. Pat. No. 4,594,363, may be added to aid in fixed or permanent base penetration. Ammonia and ammonium hydroxide are preferred.

When trying to maximize the extent of swelling, it is preferable that the one or more swelling agents are added after providing that no substantial polymerization of monomer is occurring. The amount of swelling agent can be less than, equal to or greater than the amount needed to provide for complete neutralization of the core. Preferably, the amount of swelling agent is in the range of from 75 to 300



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percent, more preferably in the range of from 90 to 250 percent based on the equivalents of the functionality in the core capable of being neutralized. It is also preferable to add the one or more swelling agents to the multistage emulsion polymer while the multistage emulsion polymer is at an elevated temperature, preferably at a temperature within 10° C. of the shell polymerization temperature. Swelling is generally very efficient under conditions of elevated temperature, in the presence of monomer and no substantial polymerization occurring. Under these conditions, swelling is generally complete within 30 minutes, preferably within 20 minutes, most preferably within 10 minutes of adding the one or more swelling agents.

The core polymer of the multistage emulsion polymer swells when the core is subjected to a basic swelling agent that permeates the shell to at least partially neutralize the hydrophilic-functionality of the core, preferably to a pH of at least about 6 to at least about 10, and thereby result in swelling by hydration of the hydrophilic core polymer. The swelling, or expansion, of the core may involve partial merging of the outer periphery of the core into the pores of the inner periphery of the shell and also partial enlargement or bulging of the shell and the entire particle overall.

When the swollen multistage emulsion polymer is dried, water and/or swelling agent are removed from the central region of the swollen multistage emulsion polymer, the core tends to shrink and a void develops, the extent of which depends upon the resistance of the shell to restoration to its previous size. This resistance of the shell restoring itself to its previous size is critical for minimizing the dry bulk density of the swollen multistage emulsion polymer. The expansion of the core results in expansion of the shell also. As the size of the shell is restored to its previous size, the dry bulk density increases. It is desirable, therefore, to minimize the extent to which the size of the shell is restored, thereby maximizing the dry bulk density of the swollen multistage emulsion polymer.

This can be accomplished by reducing the monomer level. It is believed that the presence of monomer is helpful in facilitating the swelling of the multistage polymer, whether by plasticizing the shell, aiding in the transport through the shell or a combination thereof. However, the presence of monomer is detrimental when trying to maximize swelling and minimize the dry bulk density of the swollen multistage emulsion polymer. Accordingly, after swelling the multistage emulsion polymer in the presence of both monomer and swelling agent, it is desirable to reduce the level of monomer to less than 10,000 ppm, preferably to less than 5,000 ppm based on polymer solids. This can be accomplished by any suitable means. Preferably, the level of monomer is reduced by polymerizing the monomer. This can be accomplished by any suitable means, such as by adding one or more initiators such as those recited above. It is preferred to begin to reduce the level of monomer within 20 minutes, more preferably within 10 minutes, of adding the one or more swelling agents.

The process of the present invention is capable of producing swollen multi-stage emulsion polymers having very low bulk density. Swollen emulsion multi-stage polymers having an a particle size below 275 nm can be prepared with a dry bulk density of from 0.30 to 0.77 g/cc, preferably from 0.35 to 0.76 g/cc, most preferably from 0.40 to 0.75 g/cc. Swollen emulsion multi-stage polymers having an a particle size in the range of from 275 to 500 nm can be prepared with a dry bulk density of from 0.30 to 0.74 g/cc, preferably from 0.35 to 0.73 g/cc, most preferably from 0.40 to 0.72 g/cc. Swollen emulsion multi-stage polymers having an a particle

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size in the range of from 501 to 750 nm can be prepared with a dry bulk density of from 0.30 to 0.59 g/cc, preferably from 0.35 to 0.58 g/cc, most preferably from 0.40 to 0.57 g/cc. Swollen emulsion multi-stage polymers having an a particle size in the range of from 751 to 1,300 nm can be prepared with a dry bulk density of from 0.30 to 0.46 g/cc, preferably from 0.35 to 0.45 g/cc, most preferably from 0.40 to 0.44 g/cc.

When the swollen multistage emulsion polymers are at least partially dried to produce voided polymer particles, these voided polymer particles impart favorable properties, such as gloss, brightness and opacity to paper coating formulations to which they are added.

The voided latex particles produced by the method of the present invention are useful in coating compositions, such as aqueous-based paint and paper coatings. The voided polymer particles produced by the method of this invention impart improved gloss, brightness and opacity to paper coating formulations to which they are added. Also, the voided polymer particles produced by the method of this invention impart opacity to aqueous coating compositions, such as paints, to which they are added.

#### EXAMPLE 1

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.5 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 71.2 grams of SDS (23%) and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 10.4 grams of SDS (23%), and 20.5 grams of Plurafac® B-25-5 (Plurafac is a trademark of BASF), followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 30.3% solids content and an average particle size of 145 nm.

#### EXAMPLE 2

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.7 grams of Abex® CO-436 surfactant (Abex is a trademark of Rhone Poulenc), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 14.5 grams of Abex® CO-436, and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 1.40 grams of Abex® CO-436, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME

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was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 31.4% solids content and an average particle size of 146 nm.

## EXAMPLE 3

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.7 grams of Abex® CO-436 surfactant, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 27.0 grams of Abex® CO-436, and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 4.0 grams of Abex® CO-436, and 20.0 grams of Plurafac® B-25-5 followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.7, 31.9% solids content and an average particle size of 153 nm.

## EXAMPLE 4

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 80° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 335 grams of deionized water, 14.0 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 4.5 grams of methacrylic acid, and 364.5 grams of methyl methacrylate. From this ME, 82 grams were removed and set aside. To the remaining ME was added 7.0 grams of SDS (23%) and 241.0 grams of methacrylic acid. With the kettle water at 80° C., the ME removed from the initial ME was added to the kettle, followed by the addition of a mixture of 2.75 grams of sodium persulfate in 15 grams of deionized water. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 80° C. After the completion of the monomer feed the dispersion was held at 80° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.1, 22.1% solids content and an average particle size of 184 nm.

## EXAMPLE 5

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.7 grams of Abex® CO-436 surfactant, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 9.0 grams of Abex® CO-436,

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and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 0.90 grams of Abex® CO-436, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water was added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 31.6% solids content and an average particle size of 171 nm.

## EXAMPLE 6

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 80° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 335 grams of deionized water, 10.7 grams of Disponil® Fes-993 surfactant (Disponil is a trademark of Henkel), 4.5 grams of methacrylic acid, and 364.5 grams of methyl methacrylate. From this ME, 82 grams were removed and set aside. To the remaining ME was added 5.40 grams of Disponil® Fes-993 and 241.0 grams of methacrylic acid. With the kettle water at 80° C., a mixture of 50 grams of deionized water and 10.0 grams of Plurafac® B-25-5, followed by the ME removed from the initial ME, followed by a mixture of 2.75 grams of sodium persulfate in 15 grams of deionized water were added to the kettle. The reaction mixture was stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 80° C. After the completion of the monomer feed the dispersion was held at 80° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.1, 21.5% solids content and an average particle size of 161 nm.

## EXAMPLE 7

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 80° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 335 grams of deionized water, 14.0 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 4.5 grams of methacrylic acid, and 364.5 grams of methyl methacrylate. From this ME, 82 grams were removed and set aside. To the remaining ME was added 7.0 grams of SDS(23%) and 241.0 grams of methacrylic acid. With the kettle water at 80° C., a mixture of 50 grams of deionized water and 9.8 grams of Plurafac® B-25-5, followed by the ME removed from the initial ME, followed by a mixture of 2.75 grams of sodium persulfate in 15 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 80° C. After the completion of the monomer feed the dispersion was held at 80° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 21.9% solids content and an average particle size of 220 nm.

## EXAMPLE 8

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer,

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thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.85 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 15.0 grams of SDS (23%) and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 1.75 grams of SDS (23%), and 10.0 grams of Plurafac® B-25-5, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.9, 31.9% solids content and an average particle size of 349 nm.

## EXAMPLE 9

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 5.25 grams of Disponil® Fes-993, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 11.5 grams of Disponil® Fes-993 and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 0.4 grams of Disponil® Fes-993, and 20.5 grams of Silwet® L-7001 (Silwet is a trademark of Witco), followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 31.6% solids content and an average particle size of 401 nm.

## EXAMPLE 10

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 80° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 335 grams of deionized water, 1.0 gram of Abex® CO-436, 4.5 grams of methacrylic acid, and 364.5 grams of methyl methacrylate. From this ME, 82 grams were removed and set aside. To the remaining ME was added 2.80 grams of Abex® CO-436 and 241.0 grams of methacrylic acid. With the kettle water at 80° C., the ME removed from the initial ME, followed by a mixture of 2.75 grams of ammonium persulfate in 15 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 80° C. After the completion of the monomer feed the dispersion was held at 80° C. for 15 minutes, cooled to 25° C. and filtered to

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remove any coagulum. The filtered dispersion had a pH of 3.0, 22.2% solids content and an average particle size of 328 nm.

## EXAMPLE 11

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.8 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 51.5 grams of SDS and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 25.0 grams of SDS, and 20.5 grams of Plurafac® B-25-5, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 31.6% solids content and an average particle size of 94 nm.

## EXAMPLE 12

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.8 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 51.5 grams of SDS and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water, 25.0 grams of SDS(23%), and 20.5 grams of Silwet® L-7210, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.9, 31.5% solids content and an average particle size of 81 nm.

## EXAMPLE 13

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 6.65 grams of sodium dodecylbenzenesulfonate (SDS, 23%), 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 62.6 grams of SDS(23%) and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 20.2 grams of SDS(23%), followed by the ME removed from the initial ME, followed by a mixture

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of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The reaction mixture was stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 3.0, 30.6% solids content and an average particle size of 91 nm.

EXAMPLE 14

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2260 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.70 grams of Abex® CO-436, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 23.0 grams of Abex® CO-436 and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 8.0 grams of Abex® CO-436, followed by the ME removed from the initial ME, followed by a mixture of 2.75 grams of ammonium persulfate in 40 grams of deionized water were added to the kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 28.7% solids content and an average particle size of 80 nm.

EXAMPLE 15

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 17.2 grams of Abex® CO-436, 520.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 3.0 grams of Abex® CO-436, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the kettle. The ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 30.7% solids content and a average particle size of 87 nm.

EXAMPLE 16

A core was prepared as follows: A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1760 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. A monomer emulsion (ME) was prepared by mixing 720 grams of deionized water, 2.7 grams of Abex® CO-436, 10.0 grams of methacrylic acid, and 780.0 grams of methyl methacrylate. From this ME, 164 grams were removed and set aside. To the remaining ME was added 14.5 grams of Abex® CO-436, and 510 grams of methacrylic acid. With the kettle water at 86° C., a mixture of 160 grams of deionized water and 3.0 grams of Abex® CO-436, followed by the ME removed from the initial ME, followed by a mixture of 5.5 grams of sodium persulfate in 40 grams of deionized water were added to the

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kettle. The contents of the kettle were stirred for 15 minutes. The remaining ME was then fed to the kettle over a two hour period at 85° C. After the completion of the monomer feed the dispersion was held at 85° C. for 15 minutes, cooled to 25° C. and filtered to remove any coagulum. The filtered dispersion had a pH of 2.8, 31.3% solids content and an average particle size of 118 nm.

The dry bulk density, as used herein, and in the appended claims, was determined according to the following procedure. To a 50 milliliter ("ml") centrifuge tube was added 6.3 grams of polymer solids. Deionized water was added to the centrifuge tube to provide a total of 35 grams ("g") of material in the centrifuge tube which corresponds to 18 percent by weight of polymer solids. The tube was placed in a centrifuge spun at 18,000 revolutions per minute for 120 minutes. The supernatant was decanted and weighed. The dry density was then determined by the following equations:

Dry Density=

%POLY=1-%H2O

% H2O =  $\frac{V_{H2O}}{V_{H2O} + V_P} = \frac{(V_T - S_{H2O}) \times F_R - V_P}{(V_T - S_{H2O}) \times F_R}$

$V_{H2O} = (V_T - S_{H2O}) \times F_R - V_P$

$V_P + V_{H2O} = (V_T - S_{H2O}) \times F_R$

$F_R = \frac{V_P + V_{H2O}}{V_P + V_{H2O} + I_{H2O}} = \frac{V_P + V_{H2O}}{\text{Hard Pack}}$   
 $\text{Hard Pack} = V_T - S_{H2O} = \frac{V_P + V_{H2O}}{F_R}$

where:

- W<sub>T</sub>=total weight in tube=35.0 grams
- V<sub>H2O</sub>=Volume of water inside the particles
- I<sub>H2O</sub>=Interstitial water volume
- d=polymer density=measured 1.084 g/cc
- V<sub>P</sub>=Polymer volume (6.3 g/1.084 g/cc=5.81 cc)
- V<sub>T</sub>=total volume in tube=35 g-6.3 g solids=28.7 g or cc  
water+5.81 cc polymer=34.51 cc
- S<sub>H2O</sub>=volume of supernate=weight of supernate
- %H2O=Percent water inside particles
- %POLY=Percent polymer in particles
- F<sub>R</sub>=Packing constant, which is a correction corresponding to the fraction of volume solids in the hard pack. The following packing constant values were used based on the particle size of the polymer sample:

Particle Size Range (nm)	F <sub>R</sub>
<275	0.611
275-500	0.624
501-750	0.638
751-1300	0.645

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The values of the packing constants used were based on density determinations (as described above) for unswollen polymer particles such that  $V_{H_2O}$  is zero. The packing constant,  $F_R$  is defined as:

$$F_R = \frac{V_P + V_{H_2O}}{V_P + V_{H_2O} + I_{H_2O}} = \frac{V_P + V_{H_2O}}{\text{Hard Pack}} = \frac{V_P}{\text{Hard Pack}}$$

$V_P$ =Polymer volume (6.3 g/1.084 g/cc =5.81 cc)  
 $I_{H_2O}$ =Interstitial water volume=( $W_T - S_{H_2O} - 6.3$  g)/1.0 g/cc  
 $W_T$ =total weight in tube=35.0 grams  
 $S_{H_2O}$ =weight of supernate

Using the above expression the packing constants were determined for several polymer samples having average particle sizes in the range of from about 200 nm to 1275 nm.

Sample #	P.S. (nm)	$S_{H_2O}$	$V_P$	$I_{H_2O}$	$V_P + I_{H_2O}$	$F_R$
1	213	25.0	5.81	3.70	9.51	0.611
2	440	25.2	5.81	3.50	9.31	0.624
3	650	25.4	5.81	3.30	9.11	0.638
4	1275	25.5	5.81	3.20	9.01	0.645

All particle sizes reported herein were measured using a Brookhaven BI-90 Particle Sizer and are reported as an average particle size.

EXAMPLE 17

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 190.5 grams of the core prepared in Example 1. A monomer emulsion (ME I) which was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS(23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From this ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.5%, a pH of 10.0, and a particle size of 404 nm. An acid titration showed good core encapsulation with only 4.0%

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core acid titratable. The dry density of this polymer was determined to be 0.6189 g/cc.

EXAMPLE 18

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 191.0 grams of the core prepared in Example 2. A monomer emulsion (ME I) which was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.4%, a pH of 9.9, and a particle size of 440 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density was calculated to be 0.6077 g/cc.

EXAMPLE 19

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 3. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of

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deionized water was added to the kettle and the batch is cooled to 85° C. When the contents of the reactor reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.3%, a pH of 10.2, and a particle size of 370 nm. An acid titration showed good core encapsulation with only 2.5% core acid titratable. The dry density was calculated to be 0.6466 g/cc.

## EXAMPLE 20

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1400 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 271.5 grams of the core prepared in Example 4. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the kettle is allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The contents of the reactor were held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 29.5%, a pH of 10.2, and a particle size of 525 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.5735 g/cc.

## EXAMPLE 21

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and

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was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.3%, a pH of 10.2, and a particle size of 577 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.5605 g/cc.

## EXAMPLE 22

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 279.9 grams of the core prepared in Example 6. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.6%, a pH of 10.1, and a particle size of 515 nm. An acid titration showed good core encapsulation with only 2.5% core acid titratable. The dry density of this polymer was determined to be 0.5979 g/cc.

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## EXAMPLE 23

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 274.0 grams of the core prepared in Example 7. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the batch was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.6%, a pH of 10.3, and a particle size of 650 nm. An acid titration showed good core encapsulation with only 5.4% core acid titratable. The dry density of this polymer was determined to be 0.5804 g/cc.

## EXAMPLE 24

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 8. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, and 1.5 grams of allyl methacrylate. From ME II, 114 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When

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the temperature of the kettle reached 85° C., the held back portion of ME II (114 grams) was added to the reactor followed by the addition of 38 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The kettle was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.6%, a pH of 10.4, and a particle size of 1235 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.4670 g/cc.

## EXAMPLE 25

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.9 grams of the core prepared in Example 9. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, 3.0 grams of linseed oil fatty acid and 1.5 grams of allyl methacrylate. From ME II, 114 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (114 grams) was added to the reactor followed by the addition of 38 grams of ammonium hydroxide. The contents of the kettle were held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The batch was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.4%, a pH of 10.3, and a particle size of 1275 nm. An acid titration showed good core encapsulation with only 4.5% core acid titratable. The dry density of this polymer was determined to be 0.4357 g/cc.

## EXAMPLE 26

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 270.3 grams of the core prepared in Example 10. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams

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of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, and 3.0 grams of divinyl benzene. From ME II, 114 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (114 grams) was added to the reactor followed by the addition of 38 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.1%, a pH of 10.0, and a particle size of 907 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.4648 g/cc.

## EXAMPLE 27

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 11. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS(23%), and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of

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25.0%, a pH of 10.2, and a particle size of 276 nm. An acid titration showed good core encapsulation with only 4.5% core acid titratable. The dry density of this polymer was determined to be 0.6985 g/cc.

## EXAMPLE 28

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 190.5 grams of the core prepared in Example 12. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.0%, a pH of 10.2, and a particle size of 213 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.7631 g/cc.

## EXAMPLE 29

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 196.1 grams of the core prepared in Example 13. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, 720 grams of styrene, and 3.6 grams of linseed oil fatty acid. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved



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in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 24.9%, a pH of 10.2, and a particle size of 284 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.6500 g/cc.

**EXAMPLE 30**

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1620 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 2.66 grams of sodium persulfate dissolved in 21.0 grams of deionized water. This was immediately followed by 146.3 grams of the core prepared in Example 14. A monomer emulsion (ME I) was prepared by mixing 70 grams of deionized water, 4.2 grams of SDS, 15.1 grams of butyl methacrylate, 149.5 grams of methyl methacrylate, and 3.36 grams of methacrylic acid and was added to the kettle at a rate of 4.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 133 grams of deionized water, 2.7 grams of SDS, and 504 grams of styrene. From ME II, 64 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 8.8 grams/minute and a mixture of 1.3 grams of sodium persulfate dissolved in 60 grams of deionized water was co-fed to the reactor at a rate of 1.50 grams/minute. After 10 minutes the rate of ME II was increased to 17.5 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 5.6 grams of 4-hydroxy TEMPO and 5.6 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reaches 85° C., the held back portion of ME II (64.0 grams) was added to the reactor followed by the addition of 26.6 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.67 grams of sodium persulfate dissolved in 14 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 24.5%, a pH of 10.2, and a particle size of 196 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.7955 g/cc.

**EXAMPLE 31**

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the

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kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 195.4 grams of the core prepared in Example 15. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reaches 85° C., the held back portion of ME II (137.0 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.2%, a pH of 10.0, and a particle size of 305 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.6690 g/cc.

**EXAMPLE 32**

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 191.5 grams of the core prepared in Example 16. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), 720 grams of styrene, and 3.6 grams of divinyl benzene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the batch was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137.0 grams) was added to the kettle followed by the addition of 42 grams of ammonium hydrox-

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ide. The kettle temperature was held at 85° C. for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.4%, a pH of 10.2, and a particle size of 334 nm. An acid titration showed good core encapsulation with only 2.5% core acid titratable. The dry density of this polymer was determined to be 0.6445 g/cc.

## EXAMPLE 33

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 199.8 grams of the core prepared in Example 1. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the batch was allowed to increase to 92° C. Upon completion of the ME II and co-feeds the batch was cooled to 85° C. (no inhibitor added). When the kettle temperature reached 85° C., the held back portion of ME II (137.0 grams) was added to the kettle followed by the addition of 42 grams of ammonium hydroxide. The kettle temperature was held at 85° C. for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.5%, a pH of 10.1, and a particle size of 320 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.7818 g/cc.

## EXAMPLE 34

(Comparative)

A 5liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 1998.0 grams of the core prepared in Example 1. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80° C. Upon completion of ME I, a

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second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. The ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the batch was allowed to increase to 92° C. When 777 grams of the ME II had been added to the kettle, 42 grams of ammonium hydroxide were added to the kettle and the ME II was continued. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92° C. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.7%, a pH of 10.1, and a particle size of 406 nm. An acid titration showed more core acid titratable (8.7%) compared to example #17. The dry density of this polymer was determined to be 0.6906 g/cc.

## EXAMPLE 35

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 1998.0 grams of the core prepared in Example 1. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. The ME II was added to the kettle at a rate of 25.0 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the batch was allowed to increase to 92° C. When 457 grams of the ME II had been added to the kettle, 42 grams of ammonium hydroxide were added to the kettle and the ME II was continued. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92° C. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 24.0%, a pH of 10.0, and a particle size of 573 nm which was an increase in particle size over Example 17 (404 nm); some aggregation of the particles was observed which may account for the increased particle size measured. The increased particle size is an indication of particle aggregation caused by an increase in the amount of core acid in the aqueous phase and indeed an acid titration showed high core acid titratable (14.4%) compared to example #17. The dry density of this polymer was determined to be 0.6367 g/cc.

## EXAMPLE 36

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux

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condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core  
 5 prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second  
 10 monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. When 777 grams of ME II had been fed to the kettle, 42  
 20 grams of ammonium hydroxide were then added to the kettle. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92°. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.8%, a pH of 10.2, and a particle size of 570 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.6364 g/cc.

## EXAMPLE 37

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core  
 40 prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190  
 50 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. When 457 grams of ME II had been fed to the kettle, 42  
 60 grams of ammonium hydroxide were then added to the kettle. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92°. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.5%, a pH of 10.2, and a

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particle size of 725 nm which was an increase in particle size over Example 21 (577 nm). The increased particle size is an indication of particle aggregation caused by an increase in the amount of core acid in the aqueous phase and indeed an acid titration showed high core acid titratable (18.5%) compared to Example 21. The dry density of this polymer was determined to be 0.6284 g/cc.

## EXAMPLE 38

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core  
 15 prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190  
 25 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. When the ME II and co-feeds were complete, 42 grams of ammonium hydroxide were then added to the kettle. The batch was held for 5 minutes at 92°. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.3%, a pH of 10.3, and a particle size of 530 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.8220  
 35 g/cc.

## EXAMPLE 39

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core  
 50 prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190  
 55 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After

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10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 1 gram of N,N-diethylhydroxylamine and 16 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.0%, a pH of 10.2, and a particle size of 580 nm. An acid titration showed good core encapsulation with only 5.0% core acid titratable. The dry density of this polymer was determined to be 0.5574 g/cc.

**EXAMPLE 40**

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 5. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the feed rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds, 42 grams of a 1% solution of 4-nitrosophenol magnesium salt in water was added to the contents of the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.8%, a pH of 10.2, and a particle size of 585 nm. An acid titration showed good core encapsulation with only 5.4% core acid titratable. The dry density of this polymer was determined to be 0.5481 g/cc.

**EXAMPLE 41**

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the

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kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 8. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, and 1.5 grams of allyl methacrylate. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of kettle was allowed to increase to 92° C. When 650 grams of ME II had been fed to the kettle, 38 grams of ammonium hydroxide were added to the kettle. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92° C. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The kettle was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.9%, a pH of 10.3, and a particle size of 976 nm. An acid titration showed good core encapsulation with only 4.4% core acid titratable. The dry density of this polymer was determined to be 0.5247 g/cc.

**EXAMPLE 42**

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 8. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 160 grams of deionized water, 3.2 grams of SDS, 600 grams of styrene, and 1.5 grams of allyl methacrylate. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of kettle was allowed to increase to 92° C. When the ME II and co-feeds had been completed, 38 grams of ammonium hydroxide were added to the kettle and the batch was held for 5 minutes. After the 5 minute hold the batch was cooled to 85° C. and a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The kettle was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.9%, a pH of 10.2, and a particle size of 1023 nm. An acid titration showed good core encapsulation with only 2.7%

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core acid titratable. The dry density of this polymer was determined to be 0.6945 g/cc.

## EXAMPLE 43

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 195.4 grams of the core prepared in Example 15. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. The ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds, 42 grams of ammonium hydroxide were added to the kettle and the batch was held at 92° C. for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.5%, a pH of 10.2, and a particle size of 232 nm. An acid titration showed good core encapsulation with only 6.4% core acid titratable. The dry density of this polymer was determined to be 0.9115 g/cc.

## EXAMPLE 44

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 195.4 grams of the core prepared in Example 15. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, and 720 grams of styrene. The ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. When 777 grams of ME II had been added to the kettle, 42 grams of ammonium hydroxide were added to the kettle. Upon completion of the ME II and co-feeds, the batch

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was held at 92° C. for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.2%, a pH of 10.2, and a particle size of 268 nm. An acid titration showed fair core encapsulation with 7.2% core acid titratable. The dry density of this polymer was determined to be 0.7688 g/cc.

## EXAMPLE 45

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 196.1 grams of the core prepared in Example 13. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS, 720 grams of styrene, and 1.8 grams of allyl methacrylate. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the reaction mixture reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 25.6%, a pH of 10.1, and a particle size of 237 nm. An acid titration showed good core encapsulation with only 2.9% core acid titratable. The dry density of this polymer was determined to be 0.6868 g/cc.

## EXAMPLE 46

(Comparative)

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2200 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 189.9 grams of the core prepared in Example 11. A monomer emulsion (ME I) was prepared by mixing 100 grams of deionized water, 6.0 grams of SDS, 21.6 grams of butyl methacrylate, 213.6 grams of methyl methacrylate, and 4.8 grams of methacrylic acid and was added to the kettle at a rate of 6.0 grams/minute at a

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temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.0 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the reaction mixture was allowed to increase to 92° C. When 822 grams of ME II had been added to the kettle, 42 grams of ammonium hydroxide were added to the contents of the kettle. Upon completion of the ME II and co-feeds the batch was held for 5 minutes at 92° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 26.1%, a pH of 10.2, and a particle size of 270 nm. An acid titration showed good core encapsulation with only 3.0% core acid titratable. The dry density of this polymer was determined to be 0.7746 g/cc.

## EXAMPLE 47

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 191.5 grams of the core prepared in Example 16. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I, a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From ME II, 137 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the batch was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (137.0 grams) was added to the kettle followed by the addition of 42 grams of ammonium hydroxide. The kettle temperature was held at 85° C. for 5 minutes. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The contents of the kettle were held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.5%, a pH of 10.2, and a particle size of 385 nm. An acid titration showed good core encapsulation with only 4.0% core acid titratable. The dry density of this polymer was determined to be 0.6226 g/cc.

## EXAMPLE 48

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux

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condenser. Deionized water, 1700 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 271.5 grams of the core prepared in Example 4. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS (23%), 10.8 grams of butyl methacrylate, 106.8 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 4.5 grams/minute at a temperature of 80°. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 190 grams of deionized water, 3.8 grams of SDS (23%), and 720 grams of styrene. From ME II, 91.4 grams were removed and set aside. The initial portion of ME II was added to the kettle at a rate of 25 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. The temperature of the kettle is allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the kettle and the batch was cooled to 85° C. When the kettle temperature reached 85° C., the held back portion of ME II (91.4 grams) was added to the reactor followed by the addition of 42 grams of ammonium hydroxide. The contents of the reactor were held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The reaction mixture was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 27.6%, a pH of 10.0, and a particle size of 525 nm. An acid titration showed good core encapsulation with only 4.4% core acid titratable. The dry density of this polymer was determined to be 0.5979 g/cc.

## EXAMPLE 49

A 5-liter, four necked round bottom flask was equipped with paddle stirrer, thermometer, nitrogen inlet, and reflux condenser. Deionized water, 2000 grams, was added to the kettle and heated to 86° C. under a nitrogen atmosphere. To the heated kettle water was added 3.8 grams of sodium persulfate dissolved in 30 grams of deionized water. This was immediately followed by 188.0 grams of the core prepared in Example 8. A monomer emulsion (ME I) was prepared by mixing 50 grams of deionized water, 3.0 grams of SDS, 12.0 grams of butyl methacrylate, 105.6 grams of methyl methacrylate, and 2.4 grams of methacrylic acid and was added to the kettle at a rate of 3.0 grams/minute at a temperature of 80° C. Upon completion of ME I a second monomer emulsion (ME II) was prepared by mixing 136 grams of deionized water, 2.7 grams of SDS, 406.5 grams of styrene, 102 grams of acrylonitrile, and 1.5 grams of allyl methacrylate. A third monomer emulsion (ME III) was prepared by mixing 24 grams of deionized water, 0.5 grams of SDS, 0.2 grams of allyl methacrylate, and 90 grams of styrene. The initial portion of ME II was added to the kettle at a rate of 12.5 grams/minute and a mixture of 1.9 grams of sodium persulfate dissolved in 75 grams of deionized water was co-fed to the reactor at a rate of 2.5 grams/minute. After 10 minutes the rate of ME II was increased to 25 grams/minute. The temperature of the kettle was allowed to increase to 92° C. Upon completion of the ME II and co-feeds a mixture of 8 grams of 4-hydroxy TEMPO and 8 grams of deionized water was added to the reaction mixture and the batch was cooled to 85° C. When the temperature of

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the kettle reached 85° C., ME III was added to the reactor followed by the addition of 38 grams of ammonium hydroxide. The reaction mixture was held 5 minutes at 85° C. After the 5 minute hold a mixture of 0.95 grams of sodium persulfate dissolved in 20 grams of deionized water was added to the kettle. The kettle was held for 30 minutes at 85° C. and then cooled to room temperature and filtered to remove any coagulum formed. The final latex had a solids content of 22.5%, a pH of 10.1, and a particle size of 906 nm. An acid titration showed good core encapsulation with only 2.0% core acid titratable. The dry density of this polymer was determined to be 0.4539 g/cc.

We claim:

1. A process for preparing emulsion polymer particles comprising:

- (a) providing an aqueous emulsion of
  - (i) multi-stage emulsion polymer, comprising a core stage polymer and a shell stage polymer, wherein the core stage polymer comprises, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core stage polymer, of hydrophilic monoethylenically unsaturated monomer, and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer; and wherein the shell stage polymer comprises, as polymerized units, at least 50 percent by weight of nonionic monoethylenically unsaturated monomer;
- (b) adding an effective amount of one or more polymerization inhibitors or reducing agents to substantially stop any polymerization;

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(c) providing monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer;

(d) adding swelling agent; and

(e) reducing the level of monomer by at least fifty percent.

2. The process of claim 1 wherein the one or more polymerization inhibitors or reducing agents are added in an amount of from 25 to 5,000 ppm based on polymer solids.

3. The process of claim 1 or claim 2 wherein the one or more polymerization inhibitors are selected from the group consisting of N,N-diethylhydroxylamine, N-nitrosodiphenylamine, 2,4-dinitrophenylhydrazine, p-phenylenediamine, phenothiazine, alloocimene, triethyl phosphite, 4-nitrosophenol, 2-nitrophenol, p-aminophenol, 4-hydroxy TEMPO, hydroquinone, p-methoxyhydroquinone, tert-butyl-p-hydroquinone, 2,5-di-tert-butyl-p-hydroquinone, 1,4-naphthalenediol, 4-tert butyl catechol, copper sulfate, copper nitrate, cresol and phenol.

4. The process of claim 1 wherein the monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer is one or more of the monomers used to prepare the multi-stage emulsion polymer.

5. The process of claim 1 wherein the monomer at a level of at least 0.5 percent by weight based on the weight of the multi-stage emulsion polymer is nonionic monomer.

6. The process of claim 1 wherein the swelling agent is selected from volatile base, fixed base, and combinations thereof.

7. The process of claim 1 wherein the level of monomer is reduced to less than 10,000 ppm based on polymer solids by polymerizing said monomer.

\* \* \* \* \*

### **CERTIFICATE OF SERVICE**

I certify that on November 4, 2015, this CORRECTED BRIEF FOR APPELLANT ORGANIK KIMYA AS was filed electronically using the CM/ECF system and served via the CM/ECF system on counsel for the Appellee, Rohm and Haas Company, as follows:

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**CERTIFICATE OF COMPLIANCE**

I certify that this CORRECTED BRIEF FOR APPELLANT ORGANIK KIMYA AS contains 11,484 words as measured by the word-processing software used to prepare this brief.

/s/ James R. Barney